PHYSICO-CHEMICAL STUDIES ON THE STRUCTURAL TRANSITIONS OF ORGANIZED ASSEMBLIES

ABSTRACT

THESIS
SUBMITTED FOR THE DEGREE OF
Doctor of Philosophy
IN
CHEMISTRY

SARA LIZ DAVID

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
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Dedicated

To

My Teacher & Mentor

Late (Dr.) Pushkin M. Qureshi

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Certificate

This is to certify that the work presented in this thesis entitled "***Charge Transfer Complexes of Non-Conventional Donors and Acceptors***", is original, carried out by Mr. Sukumar Sinha under my supervision and is suitable for submission of the award of Ph.D. degree in Chemistry of this university.

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S. Sinha.

(SUKUMAR SINHA)

Abstract

The aim of the work reported in the thesis is to study certain aspects of charge-transfer complexes of non-conventional donors and acceptors.

Molecular (Charge-Transfer) complexes are a special case of donor-acceptor interactions because in most (weak) charge-transfer complexes there is only a partial transfer of an electron (more correctly electron density) from an electron donor molecule to an electron acceptor molecule.

The attention has been given on charge-transfer complexes and solvent polarity scales based on charge-transfer complexes and certain aspects of sigma complexes which have been used in analytical studies. Though sigma complexes are not exclusively charge-transfer complexes but charge-transfer forces contribute significantly to this study. This thesis comprises of six chapters. First chapter is the General Introduction which is based on relevant literature to date.

The second chapter deals with thermodynamics of charge-transfer complexes. Diphenylamine (DPA), Indole and p-dimethylaminobenzaldehyde (p-DAB) have been proposed as non-conventional donors in their charge-transfer complexes with m-dinitrobenzene. $-\Delta H^0$ values establish the relative donicity and it is shown this was not possible for K which may give satisfactory results with closely related donors. It has been shown that in all cases there are two donor sites and the nitrogen lone pair is the expected donor site. IR studies are

complemented with UV-visible spectroscopic data to establish the relative donicity.

The third chapter deals with the isolation of charge-transfer bands of 2,4-dinitrotoluene (DNT) - diphenylamine (DPA) system both in solid state and solution state. In presence of some alkali and alkaline earth metals the charge-transfer band has been isolated again. These bands could not be isolated before. When metal ions are added to the molecular complexes in 80:20% DMSO/H_2O mixture a shift in frequency occurs. The intensity also increases sharply. It is shown that the first and second ionization potentials of the metal ions are a function of ν_{CT}.

In chapter four, a method has been generalized for the quantitative determination of some polynitroaromatics via their molecular complexes with diphenylamine. The method seems attractive for even those compounds that give the same colours with the reagent. True ε values for these classes of reactions at the optimum wavelength of 420 nm are also reported. The colorimetric method described can be applied to those systems where there is a rapid attainment of equilibrium and where conventional spectrophotometric and kinetic methods apparently fail. No satisfactory methods exist for the quantification of nitro-compounds as the colours formed are highly unstable. Moreover, since similar colours are obtained, specificity is also not possible.

Chapter five deals with the molecular complexes of organometallic donors and acceptors of very recent origin which gives multiple charge-transfer bands. Charge-transfer complex between triphenylantimony (TPA) and 1-chloro-2,4-dinitrobenzene (CDB) has been studied. The

solvent effect on CT complex has been studied also. In this chapter a new correlation between ΔE_T and Z-values of solvents has been proposed for multiple charge-transfer bands.

The sixth chapter deals with a novel way of determining 2,4-dinitrophenylhydrazine (DNPH) specifically by a kinetic analytical method. The reaction of DNPH with aliphatic amines generates a deep green colour in DMSO which fades with time to an almost colourless solution. Addition of a few μl of alkali hydroxide again generates an intense reddish-violet colour. The decomposition of this reddish-violet colour is the basis of the determination. The absorbances for decomposition of the reddish-violet colour were measured at a wavelength 500 nm and an interval of 30 seconds. By this method 4.9-14.7 ppm of DNPH can be determined. This method is superior to other colorimetric methods for polynitroaromatics where unstable colours and complete lack of specificity preclude their efficacy.

CONTENTS

LIST OF PUBLICATION

1. Determination of some polynitroaromatic compounds.
   Analytical proceedings Includings Analytical Communication, **32**, 223 (1995)
   Royal Society of Chemistry (U.K.).

2. Analysis of an important Pharmaceutical Reactant 2,4-Dinitrophenylhydrazine Part-2. A kinetic method for Specific Determination.
   Analytical proceeding Includings Analytical Communication, **32**, 431 (1995)
   Royal Society of Chemistry (U.K.).

CHAPTER - 1

GENERAL INTRODUCTION

Donor-Acceptor interactions can be divided in two separate classes *i.e.* the donor-acceptor approach to molecular interactions and donor-acceptor (charge-transfer) complexes.

Charge-transfer complexes comprise electron-donor-electron-acceptor association for which an intermolecular electronic-charge-transfer transition (or transitions) is usually observed.

The expression "Charge-transfer", used to describe these complexes, has been criticized on the ground that in many systems the contribution of charge-transfer forces to the stabilization of the ground state is negligible, and that in any case the term presupposes a valence bond description of the complex. However, the term is widely used in this sense.

1.1 HISTORICAL DEVELOPMENT :

The historical development of chemistry has led to the concept of the molecule. Although this idea has been vital, not all association of atoms conform to the concept. The anomalous "unsaturated valencies" or "residual affinities" of an earlier phase in organic chemistry are a reflection of our inadequate description, rather than the implied peculiarities of chemical interaction. All molecules interact with other molecules, but for the most part the intermolecular forces involved are small compared with the inter-atomic forces within molecules, and there is no problem in defining the molecule and concluding that intermolecular forces are "non-chemical' in the sense that they do not require a description in terms of classical covalent or ionic bonding. Nevertheless, while not being immediately amenable to description in terms of ionic

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1.3. MULLIKEN'S THEORY :

Mulliken's [12,13,14,16-20] valence bond (resonance) description of a weak complex formed between electron donors and electron acceptors is treated here in some detail. It provides a very adequate explanation of the characteristic electronic absorption in terms of an intermolecular charge -transfer transition. At the same time it is felt by some workers that the importance of charge-transfer forces in stabilizing the ground state of such complexes has been exaggerated [21-26]. It has been suggested, that an appreciable part of their stability may be the result of back-coordination.

Relatively weak interactions between an electron donor (D) and an electron acceptor (A) can be described in terms of a wave function of the form :

$$\psi_N(AD) = a\,\psi_0(A,D) + b\psi_1(A^- -- D^+) \qquad .....(1)$$

The acceptor and the donor may be in general molecules-ions, atoms or atom-ions, with the restriction that they are both in their totally symmetric ground state. The wave function (ψ_0) has been termed by Mulliken as the "no-bond" function. It corresponds to the structure of the complex in which binding from such results such "Physical" forces such as dipole-dipole and dipole-induced dipole interaction, London's dispersion forces, and hydrogen bonding. The wave function (ψ_1) has been termed the "dative" function. This corresponds to a structure of the complex where one electron has been completely transferred from the donor to the acceptor. In

case where A and D are neutral, this will involve covalent bonding between the odd electrons in A^- and D^+. In general, this bonding will be relatively weak because of the large separation of A and D.

It is therefore expected that charge-transfer forces will exist between like components, although they might be expected to be relatively weak since generally a strong Lewis acid will show only weak Lewis base properties. There are some exceptions, however, for example, the large polycyclic aromatic hydrocarbons should behave as strong acids and strong bases.

For simplicity the case is considered where there is only a single transition extra to the absorptions corresponding to the component moeities of the complex. This absorption arises from the excitation from the ground state of the complex ψ_N to the excited state ψ_E. For a weak interactions this transition is effective from the structure $\psi_0(A,D)$ to the structure $\psi_1(A^- - D^+)$ i.e. it is an intermolecular charge-transfer transition involving a one-electron jump from D to A. It is sometime for this reason that complexes which give rise to this transition have been called charge-transfer complexes. It must be reemphasized that the contribution of the charge-transfer structure in the ground state is usually very small *i.e.* b/a in equaiton (1) is small.

An alternative approach to the energetics of the intermolecular charge-transfer has been made, particularly by Dewar and his co-workers [21,27-31], using a simple molecular orbital description. For weak interactions the problem has been treated using perturbation theory [21]. For such systems the interaction energies for the ground state are small compared with the transition energies

to excited states of the complex, in particular the intermolecular charge-transfer excited states. Each such transition may be considered as arising from the transfer of an electron from a filled orbital in the donor to the filled orbital in the acceptor. For a single charge-transfer band, or for the lowest energy charge-transfer band in cases where multiple transitions are observed in complexes, this is generally assumed to involve the highest occupied molecular orbital (HOMO) of the donor and the lowest empty molecular orbital (LEMO) of the acceptor (Fig. 1.1)

More detailed treatment has been given by Murrell [32,33] who has attempted to demonstrate a relationship between the stability of charge-transfer complex and the intensity of charge - transfer band.

The free electron model for conjugated molecules, which was developed by various workers including Kuhn [34, 35] and Bayliss [36-39] treats the π-electrons in a conjugated molecule as a free electron gas which moves in the potential field of the molecule. This concept has been applied to charge-transfer complexes by Shuler [40], and by Boeyens [41]. Both authors have used the simplified one dimensional case rather than the more complicated three dimensional case.

For simple linear molecule, the electron energies may be represented by horizontal lines in a square well potential as in Fig. 1.2. The height of the sides of this well (V) corresponds to the energy of the K electrons plus the zero point energy. For two such molecules, say an electron donor (D) and an electron acceptor (A), which interact, the one dimensional model may be represented as

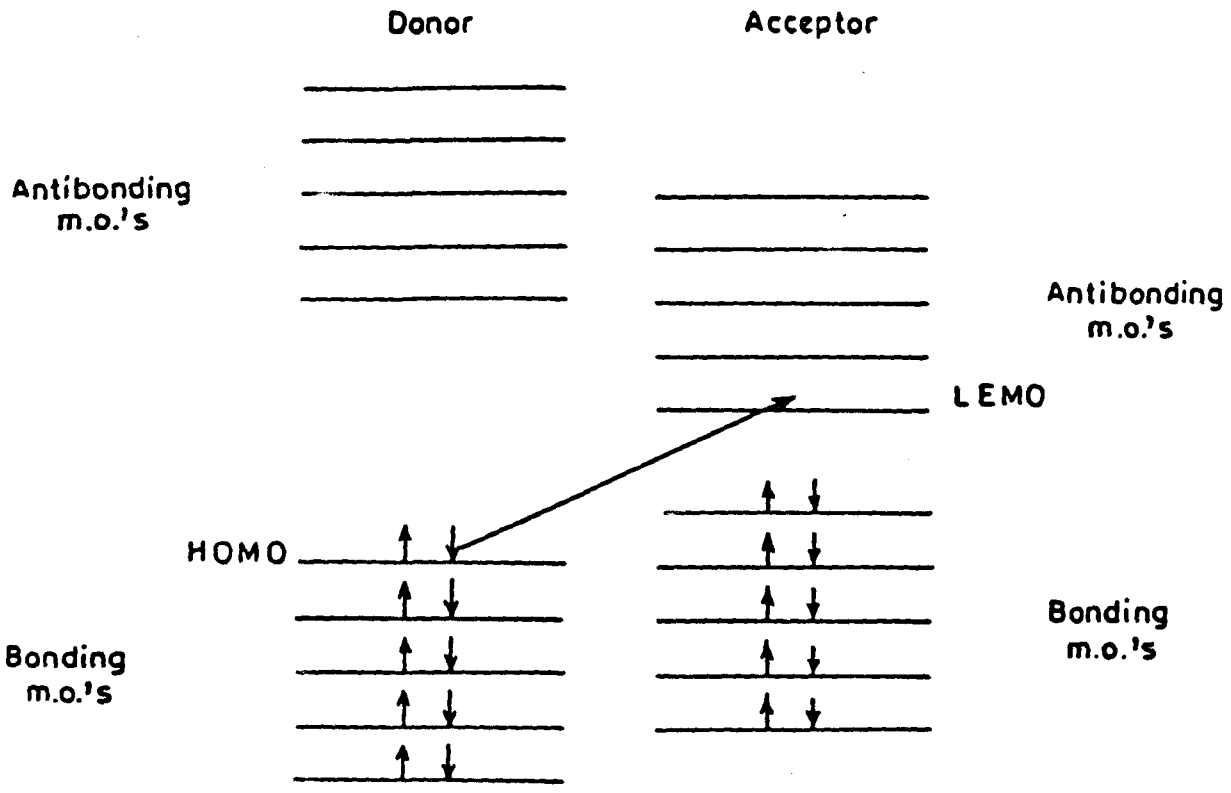


Figure 1.1 : Lowest charge-transfer transition represented as the transference of an electron from the highest-occupied molecular orbital (HCMO) of the donor to the lowest-empty molecular orbital (LEMO) of the acceptor.

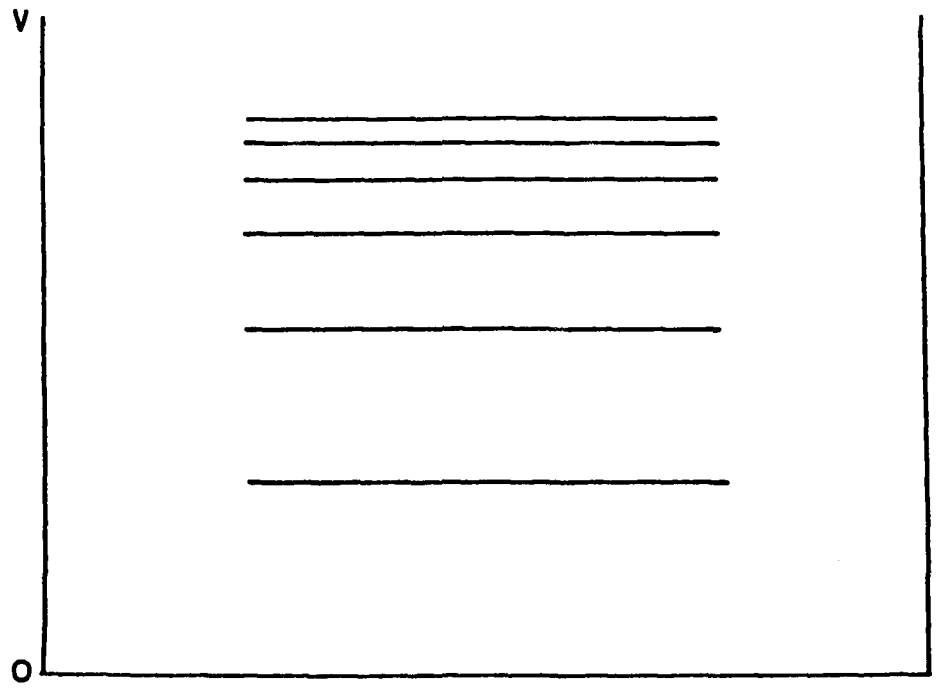


Figure 1.2 : A one dimensional potential model for a linear conjugated molecule.

a double minimum potential (Fig. 1.3). The potential barrier (of height V^{AD} relatively to molecule D) and width d, is an inverse measure of the delocalization of electron between D and A. The lowering the potential of D from V^{D} to V^{AD} becomes greater as the electron affinity (E^{A}) of A increases and the ionization potential (I^{D}) of D decreases. The width of the potential barrier (d) can be related to the intermolecular distance between A and D.

Figure 1.4 shows the change that occurs in the spectrum of iodine when it is dissolve in n-heptane and then ethanol is added (ethanol is transparent upto 220nm). The peak of the $C_2H_5OH.I_2$ CT band is marked in the figure, and the position of the shifted visible absorption band of I_2 in the complex (a transition to a locally excited state) is also indicated. The contact CT band appears as a long wavelength shoulder on the ultra-violet iodine band when I_2 is dissolved in heptane. It is felt by some authors that the importance of CT force in stabilizing the ground state of such complex has been exaggerated.

1.4. MULTIPLE CHARGE-TRANSFER BAND :

We can see from Table 1.1 that the intensity of CT spectra of the iodine-benzene complex is very large and that both the K value and the value of $-\Delta H$ increase proportionately with increasing size of electron donor hydrocarbons. However, the intensity of the CT spectra is inversely proportionate with increasing donor size. In particular, CT spectral intensity of the anthracene-iodine complex seems to be weaker than that expected from the assumption that the CT spectra may borrow much of their intensity from strong

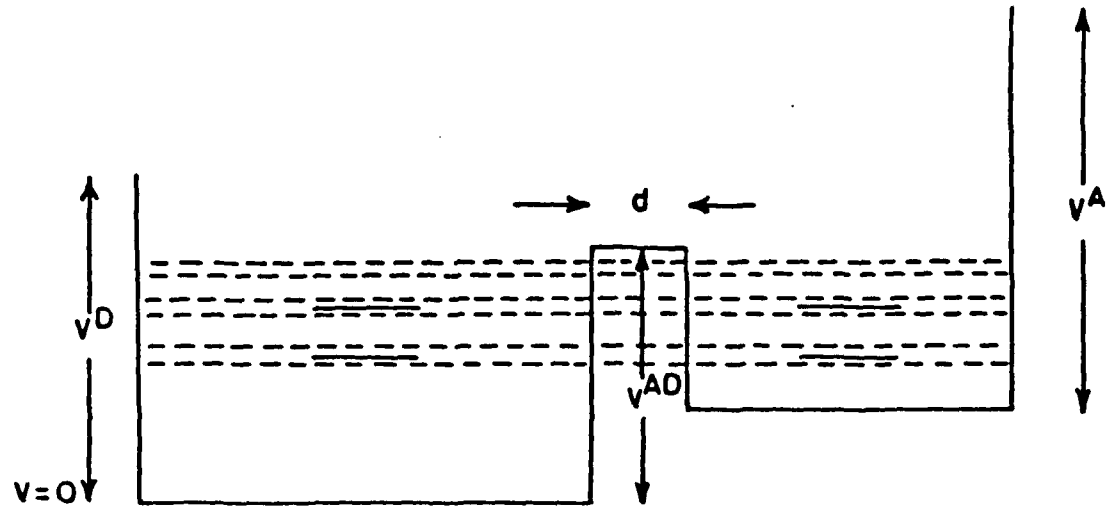


Figure 1.3 : A one-dimensional model for a charge-transfer complex of two linear conjugated molecules. The potential barrier corresponds to the non-conjugated linkage. The dotted lines show the resulting splitting of the potential energy levels.

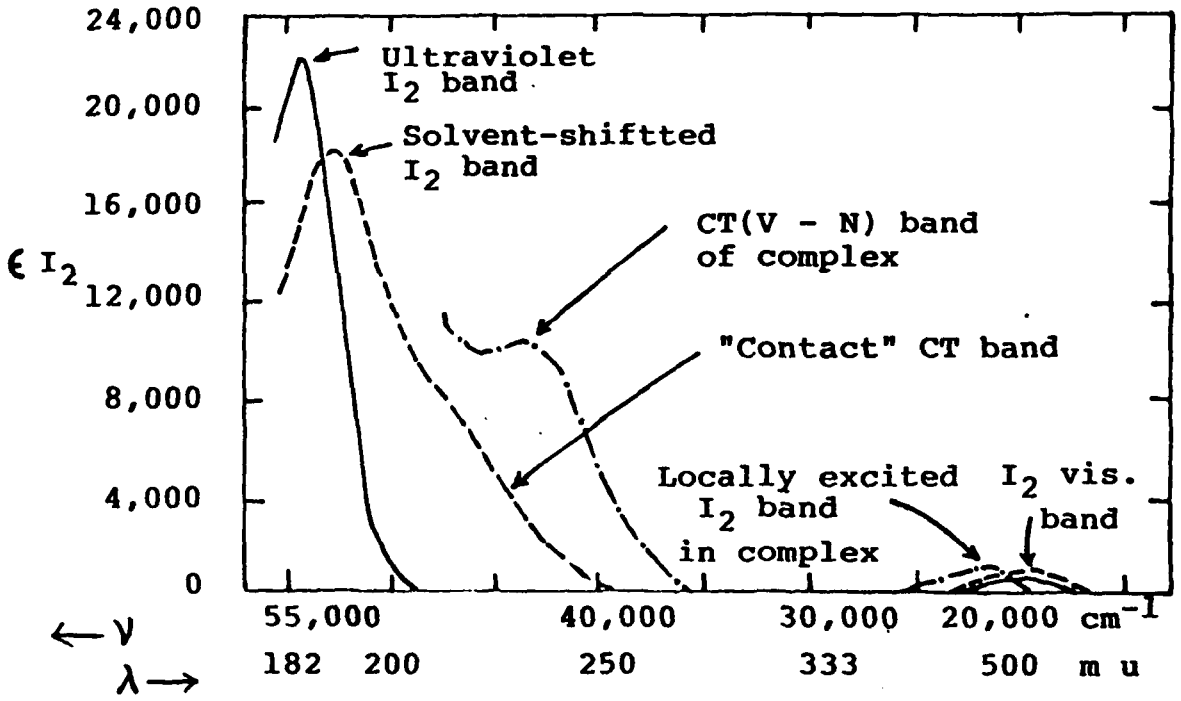


Figure 1.4 : The apparent molar absorptivity of I_2 vapor and of I_2 and EtOH. I_2 in n-heptane, Here - is for I_2 vapor, --- for I_2 in n-heptane, and -.-.- for I_2 in n-heptane with 3.4 M ethyl alcohol.

absorption bands of the donor itself. The assumption is valid because these catacondensed hydrocarbons have several lower states allowed strongly from the selection rule. In connection with this problem Murrell [42] proposed the following discussion. Generally the MO's of aromatic hydrocarbons spread over the whole molecule so that the overlap between the electron donor orbital and the accepting (σ, π of the I2 molecule) orbital becomes smaller for large hydrocarbons than for smaller ones. As a result, the CT intensity of the iodine complex with large hydrocarbons results in a weaker intensity compared with that of the complexes with small size hydrocarbons. At the same time the stability of the complexes should decrease with increasing donor size of hydrocarbons, as CT theory suggests. However, K and $-\Delta H$ values turn out to be larger with increasing size of the hydrocarbons, *i.e.*, complexes become stable, as Table 1.1 shows.

The main reason for these results may be as follows : when hydrocarbons increase in size there appear many MO's whose energies are not so well separated from one another. Hence it is possible that the charge transfer is also brought about from deeper MO's as well as the highest occupied MO of hydrocarbons. Thus the CT states can interact with the ground non bonding state, resulting in greater stabilization of the ground state. As a net result the complex become more stable as the ring size of hydrocarbon become larger. The CT bands caused by the charge-transfer from deeper donor orbitals will be hidden under the absorption bands caused by the donors or acceptors themselves. Multiple CT bands, especially two CT bands, have been reported by many workers[43]

TABLE 1.1

SPECTROSCOPIC AND THERMODYNAMIC DATA OF IONIC COMPLEXES WITH SOME AROMATIC HYDROCARBONS

Donor	K (Temp.) solv	ε_{CT} (λ CT_{max}) (solv)	H (solv) K cal $mole^{-1}$
Bezene	0.15(25°C)[a] CCl_4	16.400 (292 mm) (CCl_4)[a]	-1.3(Hexane)[b] (CCl_4)[c]
Naphthalene	0.25(25°C)[a] CCl_4	7.150(360 mm) (hexane)[b]	-1.8(Hexane)[b]
Phenanthrene	0.45(23°C)[d] CCl_4	7.100(364 mm) (CCl_4)[d]	--
Anthracene	3.0 (23°C)[d] CH_2Cl_2,CCl_4	~550 at 430 mm (430 mm) (CCl_4)[d]	-1.6(CCl_4)[d]

a. L.J. Andrews and R.M. Keefer; J. Am. Chem. Soc., 74, 4500 (1952).
b. J..A.A. Ketelaar; J. Phys. Rad., 15, 197 (1954).
c. R.M. Keefer and L.J. Andrews; J. Am. Chem. Soc., 77, 2164 (1955).
d. J. Peters and W.B. Person; J. Am. Chem. Soc., 86, 10 (1964).

for various kind of molecular complexes. A typical example is shown in Fig. 1.5.

1.5. U.V - VISIBLE SPECTRA

In general a complex formed between an electron donor and an electron acceptor still retains the absorptions of the components modified to a greater or lesser extent, together with one or more absorption bands characteristics of the complex as a whole. The recognition of this fact by Brackman [44] was important historically because it led to the realization that the absorption is the result of an intermolecular charge-transfer transition and not a modified transition of one or other component.

In practice the absorption characteristic of the complex in solution may not be easily observed since the complex will be partially dissociated into its component species. It may be particulary difficult to measure those absorption bands due to "Local excitation", when the interaction is between strong donor and strong acceptor. In such case the transition usually appears as a separate band considerably at longer wavelength that the absorption of the component molecules. The intensity of absorption band of a complex is usually determined as the molar absorptivity (extinction coefficient) at the wavelength of maximum absorption. A direct determination of intensity cannot normally be made because the degree of dissociation of the complex in solution is usually significant. Solid charge-transfer complexes have been studied by transmission [45-65] and reflection [56-68] spectra using specular reflection from a single crystal [68]. Soon after the

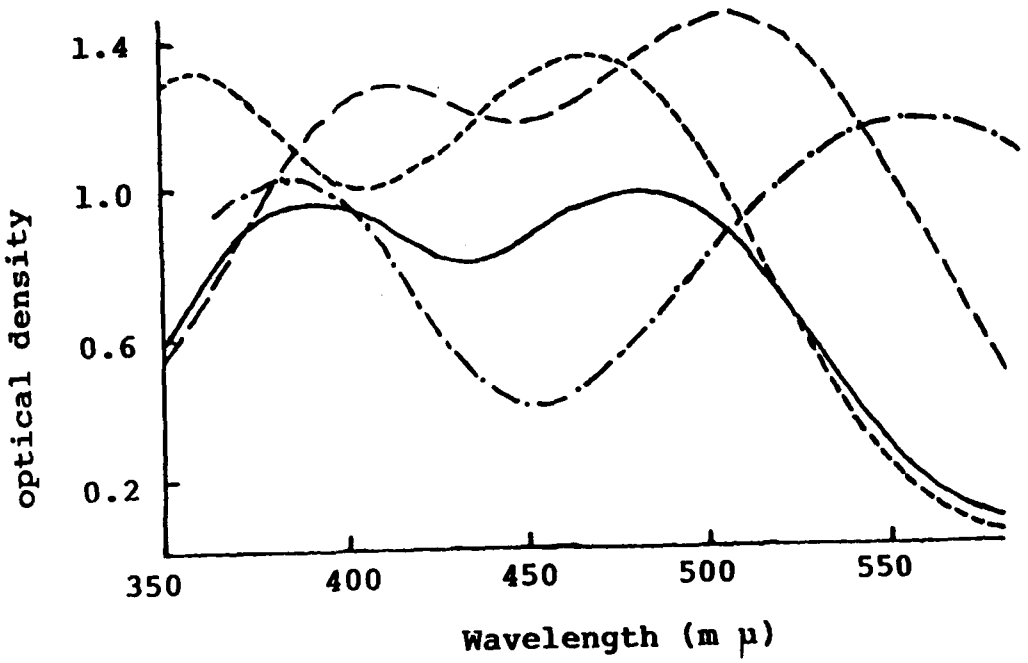


Figure 1.5 : Two CT absorption spectra observed on the chloranil-substituted naphthalene π-π complexes in CCl_4; ---- naphthalene, --- α-chlornapthalene -- α -methylnaphthalene -.-.-.- α-methoxynaphthalene. [Reproduced from A. Kuboyama; J. Chem. Soc. Japan, **83**, 376 (1962)].

publication of Mulliken's charge-transfer theory, Nakamoto [45] provided an experimental observation which could be well explained in terms of this theory, whereas the absorption of polarized light by oriented crystals and of pure aromatics shows a stronger low energy absorption when the electric vector is parallel than when it is perpendicular to the ring. The opposite obtains for the lowest energy intermolecular charge-transfer transition of a complex between the two planar molecules (Fig. 1.6).

If a number of donors are complexed with a single acceptor, a refined parabolic relationship of the form in equation (2) follows:

$$h\upsilon_{CT} = I^D - C_1 + \frac{C_2}{I^D - C_1} \qquad \text{.....(2)}$$

where C_1 and C_2 are constants for a given acceptor. This equation best correlated the data avalaible then. As the range of donors is increased, some changes in these values can be expected. Slightly prior to the application of equation (2) McConnell et al. [69] showed that there is an approximately linear relationship between I^D and υ_{CT} for complexes of iodine with the wide range of relatively weak donors.

$$h\upsilon_{CT} = I^D - E^A - W \qquad \text{.....(3)}$$

where E^A is electron affinity of the acceptor and W is dissociation energy of the charge-transfer excited state. Since the publication of that paper, similar linear relationship have been described for complexes of many other acceptors. In general,

$$h\upsilon_{CT} = a\, I^D + b \qquad \text{.....(4)}$$

when there is linear correlation between I^D and $h\upsilon_{CT}$, it is taken as a confirmation of a charge-transfer complexes, though there is no theoretical justification. There is a similar linear relationship between the electron affinity of series of acceptors, complexed with a single donor and $h\upsilon_{CT}$ of the type,

$$h\upsilon_{CT} = a\, E^A + b \qquad \text{.....(5)}$$

The electron affinity of a number of acceptors has been evaluated frcm polarographic half wave potential by the equation.

$$E^A = - E^{red}_{1/2} + 1.41 \qquad \text{.....(6)}$$

The energy of charge-transfer band is correlated with the Huckel coefficients as follwos :

$$h\upsilon_{CT}\,(A_1) - h\upsilon_{CT}\,(A_2) = B_j(A_1) - B_j\,(A_2) \qquad \text{.....(7)}$$

Kosower [70-73] has shown that $h\upsilon_{CT}$ for the complex between the iodide ion and a pyridinium ion is extremely solvent sensitive. For complexes in which the components are oppositely charged species, the ground state may be expressed as predominantly an ion pair with a small admixture of a structure involving a pyridinium radical and an iodine atom with the two odd electrons coupled, *i.e.* $a^2 << b^2$ in equation (8), in contrast to the ground state of a weak

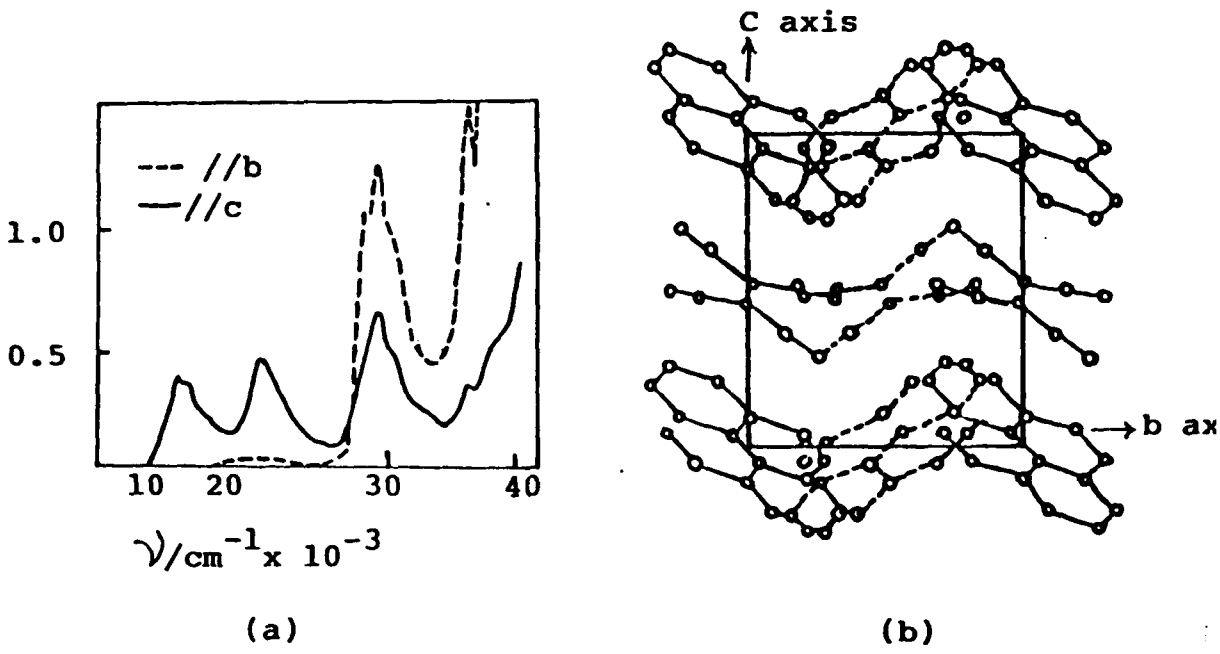


Figure 1.6 : The solid complex pyrene-tetracyanoethylene : (a) the polarized absorption spectra of a single crystal : (b) a projection of the crystal structure along the a-axis on the bc plane showing the orientation of the b- and c-axes.

complex formed of two neutral species where $a^2 >> b^2$. The excited state of the pyridinium complex will be given by equation :

$$\psi_E = a^{\#} \psi_0 (A,D) - b^{\#} \psi_1 (A^- - D^+) \quad .....(8)$$

where $a^{\#2} >> b^{\#2}$.

1.6. INFRARED SPECTROSCOPY :

The CT studies in the solids and in solution state very clearly focus our attention on the differences in the two approaches. Thus infrared measurements provide no information about relative orientation of the donor and acceptor in the complex solution. Intrared spectrum of the solid bromide-benzene complex [74] has enabled some modifications to be made to the crystal structure description determined by X-ray diffraction. The infrared spectrum which includes a bromide-bromine stretching vibration is inconsistent with the crystal structure description determined by X-ray diffraction. The infrared spectrum which includes a bromine-bromine stretching vibration is inconsistent with the crystal structure [75] having an axial configuration with chains of alternating benzene and halogen molecule, in which the halogens are equidistant from two neighbouring benzene molecules in the chain and are centres of symmetry. Person et al. [74] suggest that these conflicting observations can be reconciled if, in the crystals the halogen molecules are not, in fact, exactly equidistant from their immediate benzene neighbours in the chain, but are somewhat closer to one than the other.

The solid state studies on the tetracyanoethylene (TCNE) and hexamethylbenzene (HMB) system have been very rewarding. Two complexes with a mole ratio of 1:1 & 1:2 have been prepared [75-77]. The infrared spectrum of the two complexes are given in Fig. 1.7. The spectra of the 1:2 complex may be interpreted in terms of a structure which consists of stacks which contain sequences of D.A.D.....D.A.D.....D.A.D .....D.A.D .....molecules. In the 1:1 complex the similar absorption inthe out-of-plane infrared spectrum shows no absorption at 1295 cm^{-1} (an absorption assigned to the totally asymmetric C-CH_3 stretching mode of HMB which is forbidden in the free molecule). This is to be expected in terms of Ferguson and Matsen's [78-80] and Friedrich and Person's [81] theory, since the charge oscillation between D and A, characteristic of a vibronic interaction, is effectively zero in symmetrical D.A.....D.A..... D.A..... sequence of the 1:1 complex. However, in the 2:1 complex, the lower symmetry of the environment of the donor molecules permits the charge oscillation, and a strong absorption is observed at 1295 cm^{-1}. In contrast, the symmetry of environment of the TCNE molecule should be comparable in the 1:1 and 1:2 complexes. The similar absorption of the totally symmetric double bond mode of TCNE at 1560 cm^{-1} in the two complexes provides support for this conclusion.

The acceptors are generally classified as non acidic and acidic compounds. The former type can only form DA complexes involving electron transfer while the acidic compounds are capable of forming both the electron transfer complexes and those comprising proton donation to the donor. 2,4-Dinitrotoluene (DNT)

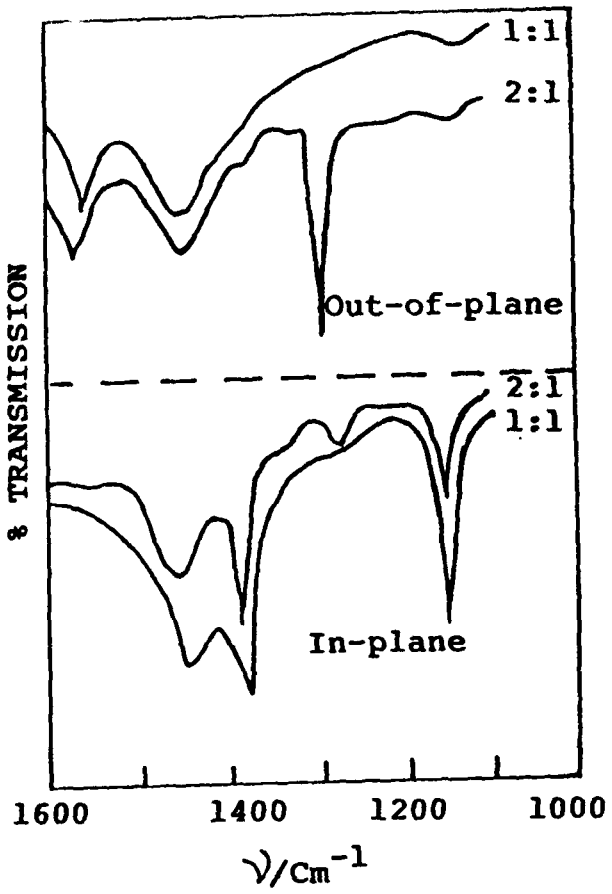


Figure 1.7 : Infrared spectra in the 1100-1600 cm^{-1} range for the 1:1 & 2:1 crystalline complexes of hexamethylbenzene and tetracyancethylene.

is a non acidic acceptor and, therefore, it is expected to display the general spectral shifts of π-π^* complexes [82]. Since the stability of these complexes arises from a shift of the electron density from the donor to the electron deficient acceptor molecule, the infrared region should record the effect of the change of electron density in the components upon the vibration of atoms within the individual molecules. Study of vibrational spectra may also reveal which parts of the molecules play an active role in complex formation.

1.7. NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY:

Just like IR, NMR spectrometry of CT complexes gives a summation of the spectra of the individual reactants. On complex formation electron density around the acceptor protons is increased and the electron density around the donor protons is decreased, giving rise to an upfield shift of the protons of the acceptor and a down field shift of the protons of the donor.

1.8. SPECTROPHOTOMETRIC DETERMINATION OF EQUILIBRIUM CONSTANT AND MOLAR ABSORPTIVITY

The formation constant is defined for the reaction

$$A + D \rightleftharpoons AD$$

By the expression

$$K = \frac{[AD]}{[A]\,[D]} \qquad \text{.....(9)}$$

Here for example, [D] is the concentration (in moles per litre) of the

donor that exists in the solution at equilibrium. If we take solution with a fixed total concentration $[A]_0$ of A but with increasing concentrations of D, equation (9) implies that the concentration [AD] of the complex AD increases as shown in Fig. 1.8 (The absorption observed may be that of the CT band or it could be absorption for a locally excited band of D or A, shifted in the complex). The absorbance A due to AD in a region in which the complex absorbs is given by Beer's Law,

$$A = \log \frac{I_0}{I} = \varepsilon [AD] b$$

Here ε is the molar absorptivity of AD and b is the length in centimetres of the absorbing path. The value of A must increase as [D] increases, as it is seen from Fig. 1.7 depending on how large K is, [AD] at maximum possible donor concentration may closely approach $[A]_0$ (region III of Fig.1.7, $K > 1.0$) or be limited to values in region II ($K \geq 0.1$) or even to region I ($K < 0.01$). In the latter case the [D] scale in Fig. 1.8 would, of course, be modified.

As a specific example, the visible spectrum of the complex between pyridine-N-oxide and I_2 is shown in Fig. 1.9. This figure illustrates the increasing absorbance near 450 nm of the complexed I_2 and the decreasing absorbance near 520 nm due to the familiar locally excited band of uncomplexed I_2 as the concentration of donor is increased, with an isosbestic point at 490 nm. The existence of this point confirms the assumption that only two species in the solution (complexed I_2 and uncomplexed I_2) absorb in this region of the spectrum.

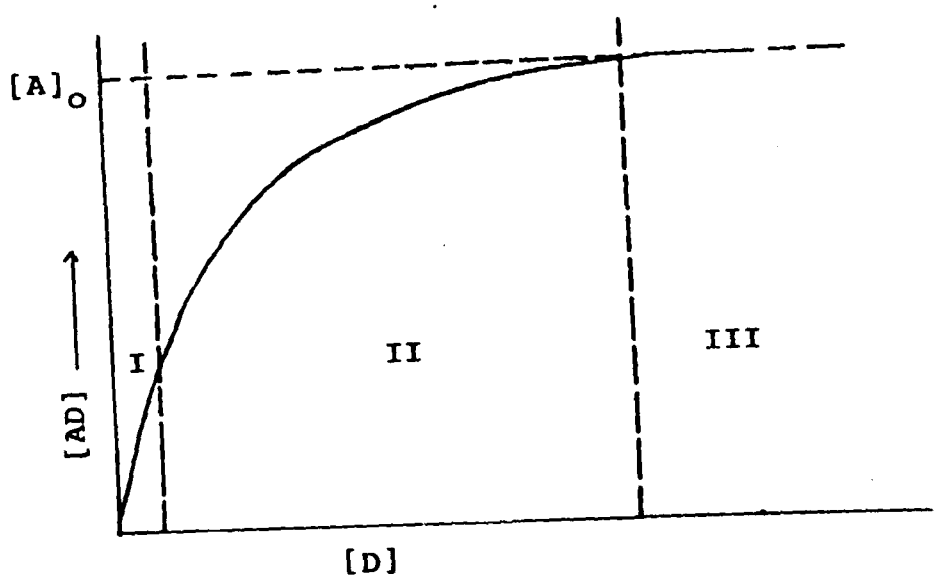


Figure 1.8 : The concentration of complex as a function of donor concentration for a fixed total acceptor concentration $[A]_0$. Regon I:[AD] is approximately a linear function of [D]. Region III : Saturation has been reached, and [AD] is constant and equal to $[A]_0$.

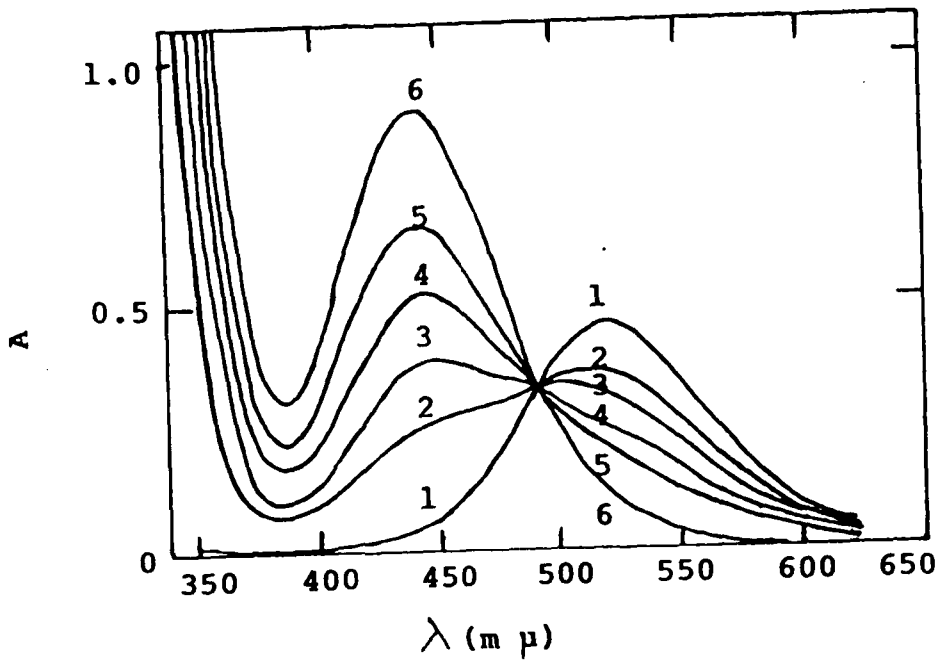


Figure 1.9 : The visible absorption spectrum of pyridine-N-oxide-iodine in carbon tetrachloride (23°C, 5-cm cell). Curve 1 is for iodine (9.550×10^{-5}M). The concentration of pyridine - N-oxide are 4.210×10^{-3}M for curve 5; curve 6 is a calculated curve for the absorption that is due solely to the complexed iodine molecule. (From t. Kubota, J. Am. Chem. Soc., **87**, 458 (1965)].

Fig. 1.9 also illustrates the problem of overlaping absorption of two species which often occurs. In principle a correction is made for the absorbance due to the uncomplexed I_2 in order that the absorbance due to the complex alone may be obtained (illustrated by curve 6 in Fig. 1.9). In practice the details of this correction may be somewhat troublesome; for example, we determine ε_A for the acceptor alone in a solvent and compute the correction A_A to be subtracted from the total absorbance A_T to obtain A, the absorbance of the complex AD. In doing so we usually assume that the absorption for uncomplexed A does not change when the solvent is changed by adding D. This assumption is at best questionable in the case of weak complexes, for which [D] has to be made rather large.

From the corrected absorbance A at a given frequency for a series of concentration [D] the values of K and ν_2 can be obtained using the method of Benesi and Hildebrand [11]. The Benesi-Hildebrand analysis starts from the assumption that only one equilibrium exists in the solution and that the constant is defined as in (9). Then using a zero superscript to denote the total concentration $[D]_0 = [D] + [AD]$, etc., we have

$$\frac{1}{K} = \frac{([D]_0 - [AD])([A]_0 - [AD])}{[AD]} = \frac{[D]_0[A]_0}{[AD]} - [D]_0 - [A]_0 + [AD] \qquad \text{.....(10)}$$

Under the usual conditions (K small, A relatively insoluble) $[D]_0$ is very much greater than $[A]_0$, in order to form enough complex : $[D]_0 >> [A]_0 > [AD]$. From Beer's Law $[AD] = A/\varepsilon_\nu l$; hence to a good approximation.

$$\frac{1}{K} = \frac{I[D]_0[A]_0\varepsilon_\nu}{A} - [D]_0 \qquad \text{.....(11)}$$

Dividing by $[D]_0\ \varepsilon_\nu$ and rearranging, we obtain the Benesi - Hildebrand equaiton :

$$\frac{b[A]_0}{A} = \frac{1}{K.\varepsilon_\nu} \cdot \frac{1}{[D]_0} + \frac{1}{\varepsilon_\nu} \qquad \text{.....(12)}$$

Here in a given experiment we know of, $b[A]_0$ and $[D]_0$; A is measured for a series of solution with varying $[D]_0$, and the results are plotted as shown in Fig. 1.10. From the slope and intercept the values of K and ε_ν can be obtained.

The above equaiton is not valid for sparingly soluble compounds because their concentration cannot be accurately determined, therefore, the Pushkin-Varshney-Kamoonpuri [83] equation was proposed to solve this problem. This equation takes the form :

$$\frac{1}{A} = \frac{1}{K\varepsilon_\nu} \cdot \frac{1}{[A]_0} \cdot \frac{1}{[D]_0} + \frac{1}{[A]_0\varepsilon_\nu}$$

.....(13)

If the plot is made of 1/A Vs $1/[D]_0$ a straight line is obtained (Fig. 1.11) and K is evaluated by dividing the intercept by slope. Therefore $[A]_0$ mutually cancels out and is not required for evaluation of $K[A]_0$ should be kept constant in all solutions.

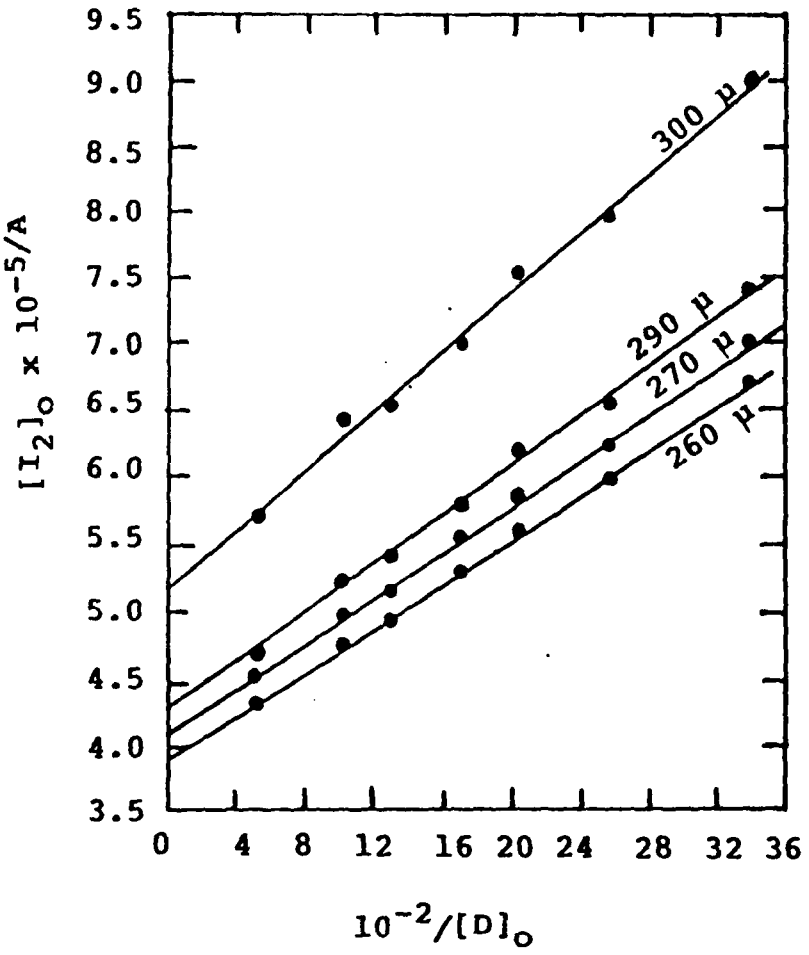


Figure 1.10 : Illustration of the use of the Benesi-Hildebrand equation to obtain K and ε_v at four wavelenths for the Triethylamine. I_2 Complex. the intercept of each line is $1/\varepsilon_v$: the slope is $(1/K\varepsilon_v)$. [From S. Nagakra. J. Am. Chem. Soc., **80**, 520 (1958)].

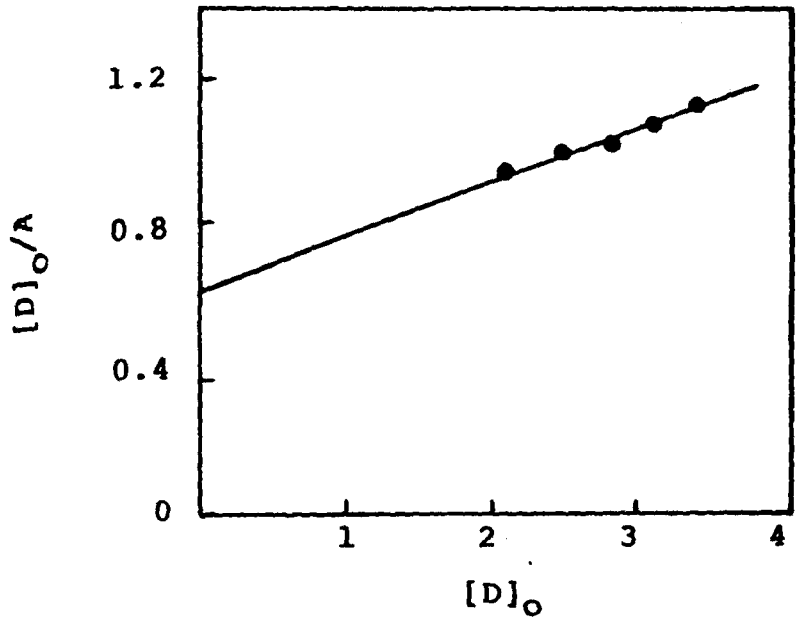


Figure 1.11 : A typical Qureshi-Varshney-Kamoonpuri plot.

1.8. DETERMINATION OF OTHER THERMODYNAMIC PROPERTIES :

We can obtain ΔH^0 from measurement of K at more than one temperature using the van't Hoff equation [84]

$$\ln K = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R} \qquad \text{.....(14)}$$

Assuming that H^0 is constant over the temperature range involved, a plot of lnk Vs I/T should then be a straight line whose slope give ΔH^0 and whose intercept is $\Delta S^0/R$. In this way the enthalpy change ΔH^0 and the standard entropy change ΔS^0 for complex formation can be obtained.

1.9. DETERMINATION OF EQUILIBRIUM CONSTANT BY IR SPECTROMETERY

Charge-transfer complexes have mainly been studied by UV-visible spectroscopy chiefly due to the possible isolation of the charge-transfer band. IR spectrometery can give an idea about the geometry of the complex. In most complexes and specially in the weaker ones the IR spectra are merely a summation of the individual spectrum. However, shifting of peaks may take place to lower or higher frequencies. The regions where there is a greater shift in electron density are the ones that give rise to more prominent peaks, enhanced intensity and greater magnitude in the frequency shifts.

IR spectrometry can also be used to determine the association constants using the usual Benesi-Hildebrand equation (12). For

this it is necessary that a peak is chosen which is not overlapped by other peaks and has maximum intensity. The transmittance is measured and converted to absorbance directly. IR spectrometry is a useful tool to distinguish between charge-transfer and hydrogen bonding. For example, if aniline is involed in hydrogen bonding the N-H vibration in the complex will move to lower frequencies while in the case of charge-transfer the reverse will be true. IR is also diagnostic of those CT complexes where there is almost complete transfer of an electron from the donor to the acceptor and highly conducting organic metals or semiconductors results. In this case there is usually no peak in the entire IR region.

1.10. DETERMINATION OF EQULLIBRIUM CONSTANT BY NMR SPECTROMETRY :

There is a difference in evaluating association constants by NMR spectrometry than in electronic or IR spectroscopy. In this case the method of Hanna and Ashbaugh [85] is used. The method is as follows : A small amount of the acceptor with a large amount of the donor is dissolved in an inert solvent like CCl_4. The acceptor concentration is kept constant while the donor concentration is varied.

The association constant is obtained according to equation.

$$\frac{1}{\Delta} = \frac{1}{K} \cdot \frac{1}{\Delta_0} \cdot \frac{1}{[D]_0} + \frac{1}{\Delta_0} \qquad \text{.....(15)}$$

Where $1/\Delta$ is plotted against $1/[D]_0$ and K and Δ_0 are evaluated from slope and the intercept.

In addition to this the Qureshi-Varshney-Kamoonpuri equation [86] proposed the outline of a method for the first time in NMR to ascertain whether the activity coefficients are unity or show deviations. The Qureshi-Varshney-Kamoonpuri equaiton takes the form

$$\frac{[D]_0}{\Delta} = \frac{1}{K} \cdot \frac{1}{\Delta_0} + \frac{[D]_0}{\Delta_0} \qquad \text{.....(16)}$$

A plot of $[D]_0/\Delta$ vs $[D]_0$ should yield a straight line with the slope giving Δ_0 and K is then obtained from the intercepts.

1.10. CLASSIFICATION OF ELECTRON DONOR AND ACCEPTOR:

In this section the classification of various kinds of charge-transfer type complexes is discussed according to charge-transfer theory because the classification of these complexes seems to be important in the interpretation of the physiochemical nature and electronic state of complexes. Mulliken [13,14] proposed this kind of detailed classification (which is generally employed by many workers in the field) from the viewpoint of the molecular electronic state. Therefore, the classification according to Mulliken nomenclature [14] is described here briefly.

ELECTRON DONOR :

The electron donor is first divided into R and E types. The former classifies the donor molecule as a radical with odd electrons, as are the usual organic neutral molecules. The E type donor

molecules are classified as *n*, σ and π type, where the electron donating orbital participating in molecular complex formation is nonbonding, σ and π orbitals represented by *n*, σ and π respectively. Typical examples are : the lone pair orbital of R_3N, σ filled molecular orbital of aliphatic hydrocarbons, and the π filled molecular orbitals of benzene, etc. for *n*, σ and π types of donor, respectively. Mulliken introduced here the terms increvalent and sacrificial, depending on whether the CT complex formation leads to an additional bond formation or causes a weakning of the bonding in the donor itself. A donor molecule of *n* type belong to increvalent donor because the transfer of an electron of lone pair electrons (which orginally did not enter into bond formation) to the vacant orbital of an acceptor brings about a new bond D^+-A^-, i.e., a lone pair electron participates in a new bond formation and it is called increvalent. On the other hand, σ and π type donors are classified as sacrificial donors. Where these donor molecules enter into CT complex formation, an electron (which occupied in most cases a highest filled molecular orbitals) is transferred to the vacant MO of an acceptor. The result here is that the bonding in the donor molecule itself is weakened and then the donor is called sacrificial type.

ELECTRON ACCEPTOR :

Following the same approach towards the classification of electron donors, electron acceptors are also divided into Q and E type. The former denotes a radical acceptor molecule with odd electrons, and the latter is the same as the case of electron donors (i.e., the E type of electrons grouped into V, σ and π types). Type

V denotes the vacant orbitals (V) acceptor, a vacant orbitals of which belongs to a key atom of an acceptor molecule; a typical example is 2P vacant orbital of boron in the molecule of BR_3. When this orbital enters into the CT type of complex formation with the amine R_3N, a new bond $\rightarrow N^+ - B \leftarrow$ is formed so that the V type of acceptor is increvalent. The acceptor orbitals of σ and π type of acceptors are, of course, σ and π type antibonding vacant molecular orbitals, if those orbitals participate in complex formation. It is evident that the bonding within the acceptor molecule itself is weakened, as has been discussed in the case of the σ and π type donor molecules. Therefore, the σ and π type of acceptors are said to be sacrificial acceptors. Table 1.2 summarizes the preceding discussion.

One can now say that there will occur various kinds of CT complexes which are classified by the combination of different donor and acceptor orbitals as shown in Table 1.2.

Although it is convenient to speak of electron donors and acceptors, one should, of course, realize that these names do not refer to fixed absolute types of molecules, but rather to modes of functioning. The same atom or molecule may funciton sometimes as a donor, some time as an acceptor, depending on its partner. When any donor atom or molecule act as an acceptor and any acceptor atom or molecule act as donor due to influence of their respective partner then that particular type of donor and acceptor are called non-conventional donor and non-conventional acceptor respectively.

Not infrequently the same molecule may function

TABLE - 1.2

CLASSIFICATION OF ELECTRON DONORS AND ACCEPTORS

DONOR TYPES

No. of Electrons	Functional Type	Structure Type	Examples(*)
Odd	Free Radical	R	Na C_2H_5, H, NO, NO_2
Even	Increvalent	*n*	R_3N, R_3N oxice, Py(pyridine), Py N-oxide, R_3P, R_2O, diaoxane, R_2S, RX; RCN, R_2CO, CO, R_3PO_4, N_2O_4, RNO_2; X-Sl, OR -Sl, CN-Sl; - NR_2, - OR, -X (intramolecular np donor island groups).
	Sacrificial	σ π	Al(aliphatic hydrocarbons) especially if cyclic (very weak); often RX, etc. Ar (aromatic) and Un (unsaturated) hydroxarbons, especially if forthified by electron- releasing groups; - C_6H_5 etc. (intramolecular p donor island groups).

(*) R may be H or an alkyl or other group; R_2 and R_3 may include two or three different R's, X' y mean F' Cl' Br, or I. Sl means solvated.

ACCEPTOR TYPES

Odd	Free Radical	Q	X, OH, NH_2, H, NO_2
Even	Increvalent	v	BR_3, AlR_3, BX_3, AlX_3, $SnCl_4$ etc; $Ag^+ClO_4^-$, Ag^+Sl, etc.; NO_2^+Sl.
	Sacrificial	σ π	X_2, XY, HX, HQ, RX, RQ, CCl_4 etc. Ar and Un, especially if polycyclic or heterocyclic, or if fortified by electron-withdrawing groups (X, NO_2, COOR, CN) as e.g. in trinitrobenzene, maleic anhydride, tetracyanoethylene; quinones; - C_6H_5 - NO_2 - COR, - COOR (intramolecular p acceptor island groups).

simultaneously as a donor and acceptor in a "2-way charge-transfer complex".

Fig. 1.12 show schematic potential curve for D and A when they are neutral even-electron molecules. They illustrate, for this case, the effects on N states, and CT spectra of the relative energies W_0 and W_1 of the pure states ψ_I and ψ_{II} of equation 17 gives better for the wave funcrion of the normal state (W) of any 1:1 DA combination.

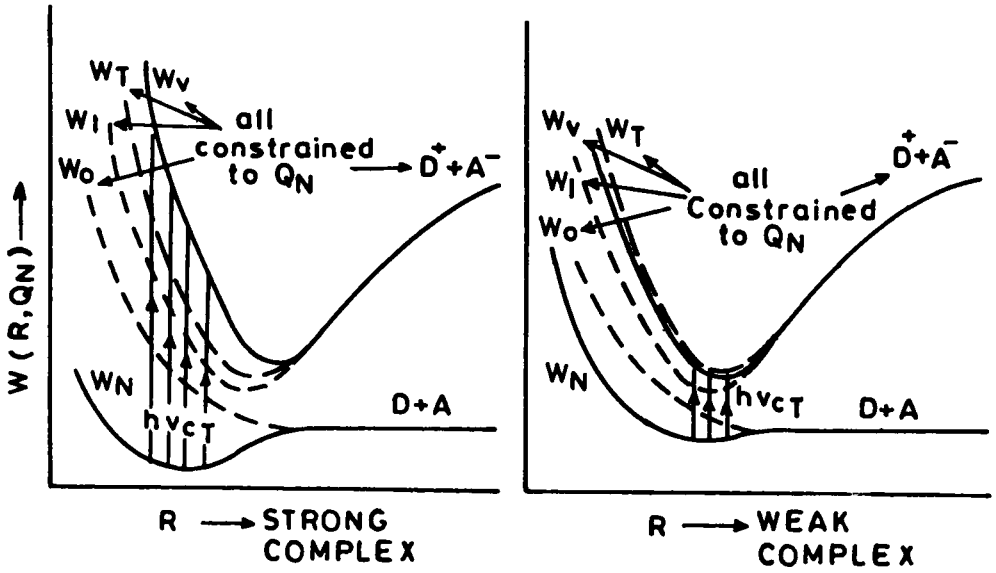
$$\psi_N = a\,\psi_0(DA) + \Sigma\, b_i\,\psi_{Ii}\,(D^+A^-) + \Sigma\, C_i\,\psi_{IIi}\,(D^-A^+) + \quad .....(17)$$

According to Mulliken, "One should speak rather of electron donor or acceptor functioning of molecules, rather than categorically of donors and acceptors."

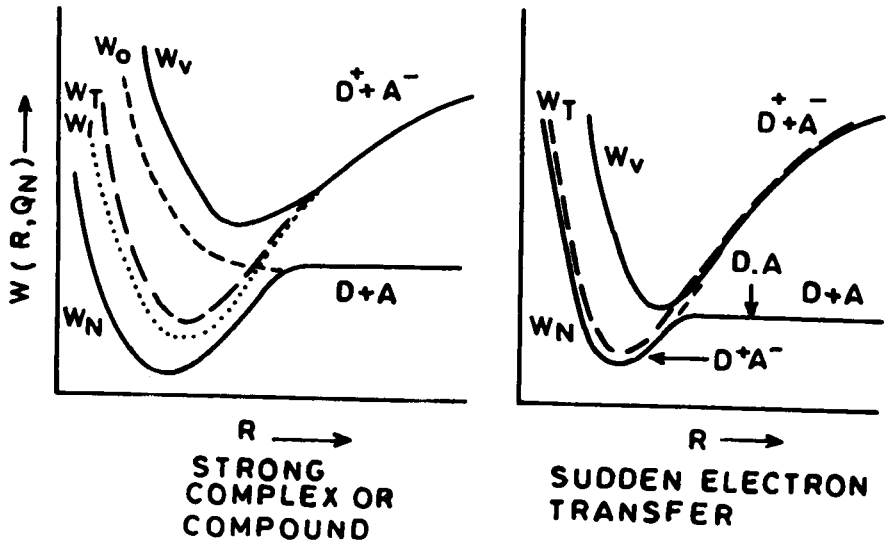
1.11. SOLVENT EFFECTS ON MOLECULAR COMPLEXES

The history of research into molecular complexes started more than a century ago. It was clear from the very beginning that liquid environment (solvent) in which the processes of molecular complexation are studied is not necessarily a neutral medium, merely filling the space between the interacting molecules. At present, it is believed that a neutral solvent is a complete idealization-placing a complex in a dense medium affects to some extent all its properties due to various physical or chemical interactions with the environment.

Inspite of the common conviction about the active role of a solvent, most early workers did not recognize this problem as one



Case I $W_1 = W_2$ approximately



Case II $W_1 < W_0$

Figure 1.12 : Schematic potential curves for the case that D and A are neutral even-electron molecules.

of first importance. The choice of solvent was frequently based on its apparent neutrality which enabled one to assume that the solute-solvent interaction would not essentially influence the complexation process. That the assumption is not correct becomes clear if one compares results obtained for such pseudo-neutral solvents with those for the vapour or gas phase [87,88]. Significance of the later data for any comparison between theory and experiment comes from the fact that almost all quantum mechanical calculation, including the theory of charge-transfer complexes [12] assume the concept of the isolated donor, acceptor and complex.

The basic idea of research on molecular association which has persisted almost without modificaton to the present, was given by Gibbs [89]. The idea consists in a careful analysis of the measured deviations from some ideal laws, such as the perfect gas law. It seems that virtually all the reported thermodynamical information pertaining to formation of complexes has been obtained by comparing experimental data with values predicted by some ideal law or combination of laws. For example either Raoult's law or Henry's law is almost universally assumed to apply to the individual species involved in a complex formation reaction in the condensed phase. For widely used spectroscopic studies an analogues assumption concerns Beer's law as well as the laws of dilute solution. Generally, one can say that direct use of the ideal laws is always followed by an assumption about the additivity of a given molecular quantity for all species involved in the reaction. In Gibb's original work the idea was clearly illustrated on the basis of dimerization results for acetic acid and nitrogen dioxide, where the

assumption that the vapour pressure deviation from the expected theoretical values can be solely attributed to the dimerization process allowed Gibbs to determine equilibrium constants and enthalpies for appropriate dimerization reactions.

Both theoretical and experimental aspects of molecular complexation processes have been widely discussed in several recent reviews [90, 91, 94-105]. As mentioned above, the present discussion is devoted to the solvent effects on thermodynamic parameters of complex; the widely investigated solvent effects on infrared, electronic, and NMR Spectra [90, 92,93] are not considered here.

The following section contains some selected experimental data illustrating the solvent effects on formation of CT complexes, it also includes the discussion of the above data on the basis of a reaction field model. Unfortunately, direct experimental data which involve both specific and physical components had to be taken into these considerations. In this connection considerable deviations, especially for some solvents, may be encountered. Apart from actual examples, this section also includes general correlation between thermodynamic parameters and reaction polarity. Despite considerable errors and scattering of experimental data, due to neglected specific interactions, a fairly good quantitative agreement with expectation of the reaction field model was obtained. These results clearly point out the use of a simple electrostatic theory in the description of solvent effects; they also provide some information on the contribution of dispersion energy to the total energy of the complex bond.

1.11.1 SOLVENT EFFECTS ON EQUILIBRIUM CONSTANTS AND RELATED THERMODYNAMIC PARAMETERS :

In this section solvent effects on thermodynamical paramters of complex formation reaction are illustrated on the basis of some selected experimental data. The data selection is not intended to be exhaustive, most data included here are chosen from those cases in which the thermodynamical parameters in the gas phase and in possibly large amounts of solvents of different polarity are reported. The experimental data concerning energy and free energy are taken directly from measurements without taking into account the competing equilibria, which introduce a considerable scattering in all correlations. This is specially important for weak complexes *in* which the specific interactions with solvent distinctly effect an effective value of equilibrium constants. The magnitude of deviation from the mean value may give a general notion about a class of solvents for which these interactions should be necessarily into account. Quantitative comparisons between experimental data and theories are seriously hindered by scarcity of data on equilibrium constants and energies of complexation measured by different investigators and with various methods are sometimes also significantly scattered.

1.11.2 EMPIRICAL PARAMETERS OF SOLVENT POLARITY :

A compilation of empirical parameters obtained by determining solvent dependent equilibrium constants, rate constants, absorption maxima in the UV-VIS, IR, NMR or ESR region, or various other quantities and used to establish scales of

solvent polarity is given in Table 1.3. A more detailed description of all the empirical solvent parameters known at present is given in a recent monograph [106].

Despite the already extensive number of 33 different solvent scales compiled in Table 1.3, only about six of them (DN, Y,Z, $ET_{(30)}$, π^* And AN), known for large number of solvents and solvent mixtures, have so far found wider application in correlation of chemical reactivities. Particularly suitable standard compounds for the determination of empirical solvent parameters are solvatochromic dyes, because measurement of absorption maxima of such dyes in solvents of different polarity is much easier to accomplish than the determination of rate or equilibrium constants of solvent dependent chemical reactions.

At present, the most comprehensive solvent scale is the $ET_{(30)}$ - scale, based on the transition energy of the solvatochromic intramolecular charge-transfer absorption of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate.

$$ET\ (KCal/mol) = hc\upsilon\ NA = 2.859 \times 10^{-3}\upsilon\ (cm^{-1}) = Z \qquad .....(17)$$

According to equation (17), the $ET_{(30)}$ value for a solvent is simply defined as the transition energy of the dissolved pyridinium-N-phenolate betaine dye measured in Kcal/mol. A high $ET_{(30)}$ - value corresponds to high solvent polarity.

TABLE - 1.3

EMPIRICAL PARAMETERS OF SOLVENT POLARITY

Symbol (Name)	Physical Quantity Measured	Solvent-Dependent Standard Process	Number of Solvents	Reference
1	2	3	4	5
FROM EQUILIBRIUM MEASUREMENTS				
(Desmotropic Constant)	Equilibrium Constant	diketo-enol tautomerism of ethyl acetoacetate at 20°C	13	107
$-\Delta G^0_{OCH3}$	Standard Free Energy	Conformation Equilibrium Between cis-and trans-2-isopropyl-5-methoxy-1,3-dioxane at 25°C	17	108
$-\Delta G^0$	Standard Free Energy	NH/OH Tautomarism Equilibrium of Schiff bases of pyridoxal-5'-phosphate at 25°C	8	109
DN(donor number)	Reaction enthalpy $-DH_{EPD}$ $Sbcl_5$	1:1 adduct formation between antimony (V) chloride as standard-EPA and EPD-solvent in 1,2-dichloroethane at 25°C	45	110,111
FROM MEASUREMENTS OF REACTION RATES				
Y(ionizing power, solvent electrophilicity)	relative rate constant k_1	S_N1 solvolysis of tert-butyl chloride at 25°C	11	112,112
N (solvent nucleophilicity)	relative rate constant k_2	S_N2 solvolysis of methyl bromide or methyl tosylate at 25°C		114,115-118
log k_1, log k_{ion}. W	rate constnat k_1	solvolysis of 2-(4-methoxyphenyl)-2-methylpropy tosylate at 75°C	15	119
X	relative rate consstant k_2	S_E2 reaction of tetramethyltin with bromine at 20°C	7	120,121
ξ (log k_2)	rate constant k_2	S_N2 Menshutkin reaction between tri-n-propylamine and methyl iodine at 20°C	78	122,123

Ω	endo-/exo-product ratio	Diels-Alder $[\pi^4_s+\pi^2_s]$ cycloaddition of cyclopentadiene to methyl acrylate at 30°C	14	123
FROM UV/VIS SPECTROSCOPIC MEASUREMENTS				
Z	molar transition energy	charge-transfer absorption of 1-ethyl-4-methoxycarbonyl-pyridinium iodid at 25°C	88	124-128
E_T, $E_T(30)$	molar transition energy	π-π^*-absorption of 2,6-diphenyl-4-[2,4,6-triphenyl-1-pyridinio-phenolate at 25°C	207	129-133
χ_R	molar transition energy	π-π^*-absorption of a positively solvatochromic undercamethine cyanine dye at 25°C	58	134
χB	molar transition energy	π-π^*-absorption of a negatively solvatochromic nonamethinemerocyanine dye at 25°C	12	135
E_T,PM	molar transition energy	π-π^*-absorption of 5-dimethylamino-2,4-pentadienal		136
ϕ(F)	wave number difference	*n*-π^*-absorption of saturated aliphatic ketones	23	137
E_K	molar transition energy	d-π^*-absorption of tetracarbonyl [N-(2-pyridylmethylene) benzylamino] molybdenum(0)	40	138
E^{SO}_T	molar transition energy	*n*-π^*-absorption of N,N-dimethylthiobenzamide S-oxide	35	139
α(solvent HBD acidity)	wave number difference	π-π^*-absorption of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-phenolate and 4-nitroanisole (1-methoxy-4-nitrobenzene), as well as further compounds	13	140,141
β(sosIvent HBA basicity)	wave number difference	π-π^*-absorption of 4-nitroaniline and N,N-diethyl-4-nitroaniline, as well as 4-nitroanisole (1-methoxy-4-nitrobenzene), as well as further compounds.	53	142,143

	absorption wave number	p-π*- and π-π*-absorption of up to nine primary solvatochromic compounds, particularly nitro-substituted arenes, as well as further compounds	95	144,145
FROM IR SPECTROSCOPIC MEASUREMENTS				
G	relative wave number difference	IR stretching vibration absorption of X=0 and X-H.....B groups (X=C,S,N,O or P; B=HBA solvent) In the gas phase and in solution	20	146, 147
B (CH_3OD) (solvent Lewis)	wave number difference	IR stretching vibration absorption of O-D in CH_3OD in the gas phase and in solution	55	148, 149
B (C_6H_5OH) (solvant Lewis basicity)	wave number difference	IR stretching vibration absorption of O-H in C_6H_5OH in the gas phase and in solution	198	150
FROM ESR SPECTROSCOPIC MEASUREMENTS				
A_N	splitting constant a^{14N}	^{14}N..HFS splitting in the ESR spectra of three dialkylaminyl oxide radicals	31	151, 152
FROM NMR SPECTROSCOPIC MEASUREMENTS				
P	relative ^{19}F-NMR chemical shift	^{19}F-NMR absorption of 1-fluoro-4-nitrosobenzene	52	153, 154
AN (acceptor number)	relative ^{31}P-NMR chemical shift	^{31}P-NMR absorption of triethylphosphine oxide	46	155-157
FROM MISCELLANEOUS MEASUREMENTS				
S	equilibrium constant, rate constant, molar transition energy	mixed parameter, calculated from various solvent dependent processes, particularly from Z-values	47	158

δ(solubility parameter)	molar energy of vapourization, E(=molar cohesive energy), and molar volume, V_M, of the solvent	δ-values are the square roots of the molar cohesion energy densities, $\delta = (-E/V_M)^{1/2}$	400	159-161
ΔI	differences of retention indices in gas-liquid chromatography	retention of selected standard compounds depending on the polarity of stationary liquid phases		162-165
P'	gas-liquid partition coefficients of selected standard solutes	distribution of different polar test-solutes (e.g. ethanol, 1,4-dioxane, and nitromethane)	75	166,167-169
ε^0(eluant strength)	liquid-solid adsorption of solutes on alumina from different solvents	adsorption energy of solvent per unit area of adsorbent with unit activity in liquid-solid chromatogaphy (ε^0=0) for *n*-pentane on alumina)	46	170, 171

1.12. SOME RECENT DEVELOPMENT IN CHARGE TRANSFER COMPLEXES :

Equilibrium measurements, have been used for the evaluation of ionization potential [172]. Though such studies leave much to be desired by way of accuracy, nevertheless they are important due to their inherent simplicity. The space interactions and reactivity have been related by studying the photoelectron and charge transfer spectra of benzobicycloalkenes [173]. Studies of micellar media are gaining a unique importance in chemistry and therefore it is interesting to note, a report shows the effect of micelles on the state and dynamics of some excited charge-transfer complexes. [174]. The formation constants of selected charge-transfer complexes have been measured using a computer controlled precision polarograph [175].

It has been shown that flavin mononucleotide forms charge transfer complex with phenols. This has been established through the use of resonance Raman spectroscopy [176]. A single crystal of the charge-transfer complex between hexaethylbenzene and tetracyanoethylene was investigated for conformational effect and for charge-transfer transitions [177]. Conducting organic charge-transfer complexes are of current importance due to their possible use as organic conductors, semiconductors and therefore, it is interesting to note that the charge-transfer salts synthesized by the reaction of tetrathiafulvalene and tetrahalo-p-benzoquinones produced highly conducting organic materials [178]. It was shown that the complexes of phenylfurans and tetracyanoethylene were π-π^* complexes [179]. In an excellent study it has been shown that

some charge-transfer complexes of tetracyanoquinodimethane can be used to prepare electrochemical electrodes which can be used over a potential region where they serve as inert electrodes [180]. Most of the organic conductors to date have been based on tetracyanoquinodimethane. Therefore it is very encouraging to note that charge-transfer compounds composed of tetrathiafulvalene and chloranil are perhaps the first highly conducting organic materials that do not contain tetacyanoquinodimethane [181]. IR spectroscopy has been used to study the degree of charge-transfer in organic conductors [182]. n-π^* charge-transfer compelxes are now systematically being studied due to the paucity of such studies on this important family of complexes. For example, the interaction of aliphatic amines and benzonitrile has been reported [183]. The solvent effects on the charge-transfer spectra of some aminoanthraquinone dyes have been reported in nine different solvents [184]. Surface enhanced Raman scattering shows that there is a charge-transfer from tetrathiafulvalene to silver and gold [185]. The formation of a charge-transfer complex between quinoline and boron tetrafluoride leads to significant changes in the ordering of electronic levels effecting fluorescence and phosphorescence [186]. The mechanism of electron transfer from dihydronicotinamide adenine dinucleotide (NADH) to p-benzoquinone derivatives has been shown to proceed via a charge-transfer complex [187]. Picosecond laser photolysis has been used to establish the charge-transer process that occurs in the dibenzocarbazole pyridine hydrogen bonded complexes as a function of structure [188]. The 1:1 and 2:1 complexes of hexamethylbenzene with

tetracyanoethylene have been studied by resonance Raman spectroscopy [189]. The colour of nitrophenyl anilines has been explained from an X-ray crystallographic study that indicates that the molecules are placed in a "head to tail" arrangement resulting in an unusual charge-transfer between two molecules of the same compound [190]. Some large electron acceptor based on various substituted quinodimethanes have been designated as acceptors for molecular metals [191]. The study of vapour-phases charge-transfer complexes is rather difficult owing to the sophistication and cost of instrumentation. It is due to this reason that not much progress has been made in this important direction. It is therefore, encouraging to note that electron energy loss spectroscopy has been used for the investigation of vapour-phase charge-transfer complexes of halogens with *n*-donors [192]. Graphite coated with viologen polymers behave as an electrode via a charge-transfer process [193]. Charge-transfer complexes have been used for the synthesis of organic ferromagnetic materials [194]. The trimethylamine-sulpher dioxide system is the only system for which reaction thermodynamics are known both in solution and gas phase. The microwave spectrum of this system has been studied in order to elucidate the structure of the complex [195]. The reaction of azoalkanes with a series of donors which are both sacrificial ($\pi^{\#}$, $\sigma^{\#}$) and increvalent gives rise to charge-transfer complexation [196]. The fluorescence spectrum of benzanilide exhibits the anomaly that its λ_{max} occurs at longer wavelength than that of its phosphorescence emission. It has recently [197] been shown that this anomaly may be due to an intramolecular charge-

transfer transition. A new approximate procedure for the determination of enthalpy of formation and formation constants of weakly bonded charge-transfer complexes has been reported and has been applied to complexes of molecular iodine and chlorinated benzenes [198]. The effect of solvent on diplole moment and charge-transfer in electron systems has been studied in N,N-dimethyl-p-nitrosoaniline [199]. ^{1}H NMR spectrometry [200] has been used to evaluate association constants for the electron donor-acceptor complexes for the complexes of indoles and substituted indoles with 1-(2,4,6-trinitrophenyl) propan-7-one. It has been suggested that both internal and external references may be eleminated in NMR determinations of fast equilibria with special reference to charge-transfer complexes[201]. The study also questions the use of tetramethylsilane (TMS) as an internal reference due to possibility that TMS may not be as inert as assumed. A new and simple development for the measurement of charge-transfer through fibre optic photometry has ben proposed [202]. The preparation and solid state characterization and X-ray crystal structure of 1:1 charge-transfer complex of tetrathiafulvalene and m-dinitrobenzene is an important land mark in the study of charge-transfer complexes of polynitroaromatics [203]. When liquid and film polymeric compositions like polyurethanes, polyehtylene glycol-115 and styrene-methacrylate-acrylonitrile copolymer are dopped with anion radical salts like NaTCNQ in the presence of crown ethers, their conductivities increase due to charge-transfer complexation [204]. A spectrophotometric assy of certain cardiovascular drugs through their charge-transfer complexes with p-chloranilic acid,

dichlorophenyl indophenol and 2,3-dichloro-5,6-dicyano p-benzequinonen has been described [205]. In an interesting study it has been shown that the tropylium cation ($C_7H_7^+$) forms donor-acceptor complexes with various benzene , napthalene and anthracene donors signified by bright coloured solutions and linear relationships with arene ionization potential [206]. Spectroscopic studies on charge-transfer complexes of trivalent phosphorus compounds like triphenyl phosphine with maleic anhydride have been carried out [207]. A conductometric tritration technique has been used for determining the stoichiometry of charge-transfer complexes inhibit ionization in polar media [208]. Mainly, complexes of iodine have been studied. Charge-transfer complexes formed by a electron donor (2,3,6,7,10,11-hexa-*n*-pentyloxytriphenylene) and a electron acceptor (2,4,7-trinitrofluoren-9-one) in non polar solvents are studied by pico-second time-resolved absorption spectroscopy based on Kerr ellipsometry [209]. Charge-transfer complexes formed between various para - substituted benzoyl chlorides and triethylamine in acetonitrile have been studied spectrophotometrically [210]. N-nitrosopyridinium cation ($PyNO^+$) forms a series of intermolecular EDA complexes with aromatic hydrocarbons which show distinctive charge-transfer absorption bands in the visible region [211]. Charge-transfer complex of arylazoactylacctones as electron donors with picric acid and 3,5-dinitrobenzoic acid as acceptors has been studied spectophotometrically [212]. Charge-transfer complexes formed by 2,4-dimethoxynapthalene with some π acceptor are studied optically [213]. The rate of back charge-transfer following

photoexcitation of ground state complexes between CLO and aromatic molecules in nitrile solvents has been studied [214]. The charge-transfer absorption and fluorescence spectra, resonance Raman spectra and equilibrium constants and molar absorptivities of the complexes between tetracyanoethylene and hexamethylbenzene (h18-HMB) or perdeuteviated hexamethyl benzene (d18-HMB) are compared [215]. Properties of "sandwich" charge-transfer (CT) complexes, composed of bis-anthracene host compounds , in which two anthracences are connected by an anthraquinone spacer, and various aromatic acceptors have been systematically studied. [216]. Charge-transfer complexes of some diazines with 1,3,5-triazine with the σ electron acceptor iodine has been investigated spectrophotometrically in $CHCl_3$ [217]. Modified spectrophotometric method for determination of some important antibiotics has been studied through charge-transfer complexation reaction with chloranil [218]. Influence of the Alkaline metal counter cations on charge-transfer complexes between methyloiologen and aromatic donors has been studied [219].

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CHAPTER - 2

THERMODYNAMICS OF CHARGE-TRANSFER COMPLEXES RELATIVE DONICITY OF DIPHENYLAMINE, INDOLE AND p-DIMETHYLAMINOBENZALDEHYDE IN THEIR REACTION WITH m-DINITROBENZENE

It has been well established that aromatic nitro compounds are capable of forming complex of the charge-tranfer type as described by Mulliken [1-3] and more work done by Dewar and Lepley has also reported the formation of such complexes [4]. Bier [5] has investigated sym-trinitrobenzene complexed with aromatic amines and hydrocarbons in chloroform. Foster and co-workers [6-8] have studied a number of nitro systems. From these works it has been determined that steric effect plays an important role in complex formation. Further, it has been shown that an increase in the number of nitrogroups in the acceptor molecule produces an increase in the degree of association as shown by the magnitude of association constants with a number of amines [8].

Diphenylamine, Indole and p-dimethylaminobenzaldehyde have been proposed as non-conventional donors in the formation of charge-transfer complex with m-dinitrobenzene. It has been shown that in all cases there are two donor sites and each nitrogen lone pair is the expected doner site.

The reaction of 2,4-dinitrotoluene with diphenylamine [9], p-dimethylaminobenzaldehyde [10], and indole has been studied in detail in these laboratories.

p-dimethylaminobenzaldehyde [11] is a useful reagent in organic analysis. It gives coloured products and also produces flurorescent [12] compounds in soslution. Since m-dinitrobenzene has important pharmaceutical properties [13-16]. Therefore, it is worthwhile to study of the thermodynamics of its charge-transfer complex.

It is usually assumed that the strength of a donor is based on

the magnitude of equilibrium constant (K) [17], though this is usually applicable only for closely related donors. However $-\Delta H^0$ is more closely related to the stabilization by the charge transfer forces and concept of the strength based on Mullikens theory [18]. Mulliken and persons are of the view that the stability of the complex as measured by k nearly always goes qualitatively in the same way as $-\Delta H^0$ [18]. The formation of a 1:1 complex has been postulated to explain certain spectral data with varying degrees of success. Benesi and Hildebrand [19] first suggested a method of calculating the association constant K and the molar absorptivity of a complex for the system :

$$A + D \underset{}{\overset{K}{\rightleftharpoons}} C.$$

The Scott [20] and Ketelaar [21] equation are also applicable for such calculations. The validity of a spectral analysis performed by these procedures has often been questioned. Variations in the value of K have been shown a dependence upon wavelength contrary to what is predicted.

In the present work, Infrared (IR) studies are complemented with UV-visible spectroscopic data to establish the relative donicity.

EXPERIMENTAL :

Diphenylamine (B.D.H., Poole, England, AR), indole (Sigma), p-dimethylaminobenzaldehyde (E. Merck Darmsdadt), m-dinitrobenzene (B.D.H. Analar) and CCl_4 (B.D.H. Analar) were used. The solids were recrystallised to constant melting point, till

they were in agreement with reported value.

All solutions were prepared in CCl_4 at room temperature. Measurements in the Ultra-violet and visible regions were made with Bausch and Lomb spectronic 1001 uv-visible spectrophotometer. The association constants were evaluated in the presence of large excess of donor concentration as compared to acceptor concentration. The temperature was maintained to $\pm 0.1^{\circ}C$. IR spectra were recorded on a Perkin Elmer instrument by the KBr disk technique.

The equilibrium constants were calculated at 400 nm by the well known Benesi-Hildebrand equation [19].

$$\frac{[A]_0}{A} = \frac{1}{K\,\varepsilon_{400}} \cdot \frac{1}{[D]_0} + \frac{1}{\varepsilon_{400}} \qquad \text{.....(1)}$$

under the condition $[D]_0 >> [A]_0$.

RESULTS AND DISCUSSIONS

Table 2.1 gives the K values at various temperatures and the $-\Delta H^0$ values, for the m-dinitrobenzene -donor complex. It is seen that at 15°C and 30°C K follows the trend :

Diphenylamine >indole>p-dimethylaminobenzaldehyde.

On the other hand $-\Delta H^0$ follows the trend :

p-dimethylaminobenzaldehyde>indole>diphenylamine.

It is readily seen that the trend is reversed.

In the case of Indole at 40°C there seems to be significant breaking of the complex and hence there is little difference between its association constants at 30°C and 40°C. Here the $-\Delta H^0$ has been

TABLE - 2.1

$-\Delta H^0$ AND K VALUES FOR THE VARIOUS m-DINITROBENZENE COMPLEXES

Donor	K(l^{-1} $mole^{-1}$ at 15°C and 30°C)		$-\Delta H^0$ (K Cal $mole^{-1}$)
	15°C	30°C	
Diphenylamine	4.17	5.00	3.0
Indole	2.67	4.44	6.0
p-Dimethylaminobenzaldehyde	2.40	4.00	6.6

evaluated with only two points on the Vant Hoff plot. It may be a questionable procedure, nevertheless, it has been very widely used [22]. The temperature at which the thermodynamics has been carried out is 15°C, 30°C and 40°C.

It is also possible that the deviation of indole at 40°C may be due to unusual concentration effects shown by indole [23].

Elecctrostatic forces may contribute significantly to K but are unlikely to contribute to $-\Delta H^0$. As mentioned earlier results based on $-\Delta H^0$ should be more correct.

When the infrared spectra of charge-transfer complexes are compared with those of the isolated molecules which form the complex, the three types of change are found to occur : (i) the vibrational frequencies in donor or acceptor (or both) may be shifted, (ii) the intensities of the bands may be changed considerably, and (iii) new low-frequency bands appear due to the vibrations of one molecule in the complex against the other. Change in the spectra of the electron acceptors and electron donors have been illustrated in the same manner as studied earlier [24-26].

IR spectra of these complexes referring exclusively to the $-NO_2$ peak alone and relating it to the Kross classification [27] have been discussed. However, I have new reinvestigated this spectra and report a detailed characterisation for DNT (free) and in its complexes.

Table 2.2 shows such an analysis. The shifts of CH_{Ar} are rather pronounced in all cases. The difference in shifts of other groups is marginal. Therefore the CH_{Ar} peak may be most diagnostic

TABLE - 2.2

CHARACTERISTICS IR FREQUENCIES OF DNT (FREE) AND ITS COMPLEXES WITH INDOLE, DPA AND pDAB in cm^{-1}

Group	DNT	DNT-Indole Complex	DNT-DPA Complex	DNT-pDAB Complex
H_20	(3500)			3240
CH_{Ar}	(3140)	(3030); Δ=110	(3040); Δ=100	(3240); Δ=120
CH_3st	(2780)	n.o.	n.o.	n.o.
$N=C_{Ar}$	(1590)	(1605); Δ=15	(1580); Δ=10	(1600); Δ=10
NO_2	(1520)	(1530); Δ=10	(1500) Δ=20	(1500); Δ=20
	(1635)sh	n.o.	(1520); Δ=15	n.o.
NO_2	(1350)	(1340); Δ=10	(1340); Δ=10	(1345); Δ=5
CH_{3bend}	(1380)	(1410); Δ=30	n.o.	n.o.
CH_{3rock}	(1040)	(1035); Δ=05	n.o.	n.o.
CN	(0840)	(910) (920) (4)	n.o.	n.o.
Unsymmetric		75		
Trisubstituted	(1610)	(1600); Δ=10	(1590); Δ=20	n.o.

Figures in parenthesis refer to the wavenumber (Cm^{-1}) at which the respective peak appears.
Δ refers to the shift in Cm^{-1} with respect to the same peak in the parent compound (DNT).

Sh = Shoulder Ar = Aromatic St = Stretch n.o. = Not observed

for this work. The trend, thus, obtained follows the same direction as $-\Delta H^0$, namely :

pDAB (ΔCH^{Ar} = 120 cm^{-1}) > indole (CH_{Ar} = 110 cm^{-1}) > PA (CH_{Ar} = 100 cm^{-1}).

Therefore results obtained from IR spectroscopy support the result obtained for $-\Delta H_0$, for UV-visible spectroscopy.

Since the CH_{Ar} or DNT is most affected, it may be assumed that maximum charge goes to the ring of DNT. And since the donors are largely *n*-donors the complexes are largely *n*-π complexes. Electron donation will, therefore, depend on the delocalization of the non-bonded electrons of the nitrogen atom, in which structural and steric factors will be dominated. It is readily seen that for widely different structural donors, $-\Delta H^0$ gives the donicity sequence and on K compared with the very large amount of data published on K only few attempts have been made to evaluate $-\Delta H^0$.

Ionisaiton potential (I^P) therefore, would be ideal parameters to define specificity. However, in most cases these are difficult to determine. In such cases the association constants (K) may be used for evaluation of donocity, even though K will depend on the acceptor used.

Plots of K (obtained in solution) for the complexes of the above donors with m-dinitrobenzene Vs their ionisation potentials are given in figure 2.1 and 2.2. All the ionization potential values are from reference [28-30]. A typical plot of $-\Delta H^0$ against ionisation potentials of same donors is given in figure 2.3. The good linearity of the graph is clear from the value of the correlation coefficient which equal to 1.0000 for all figures.

It is usually assumed that the strength of a donor is based on the magnitude of K [17], though this is usually applicable only for closely related to the stabilisation by the charge transfer forces and concept of the strength based on Mulliken's theory [18].

There has been extensive controversy in the literature about molecules having two potential donor sites as to which site is the more potential donor site as to which site is the more potential donor.

The good linearity of all plots shows that the N-atom is the more effective donor atom as an electron of this lone pair would be detached very easily.

In complexes of this type one would expect low values of K and ε because the n-π^* transition is a forbidden transition and would occur with low ε and hence lower K. This fact is explained by figures 2.1 and 2.2.

This information will help to devise method or the analytical methodology to be followed in case where there is more than one doner site.

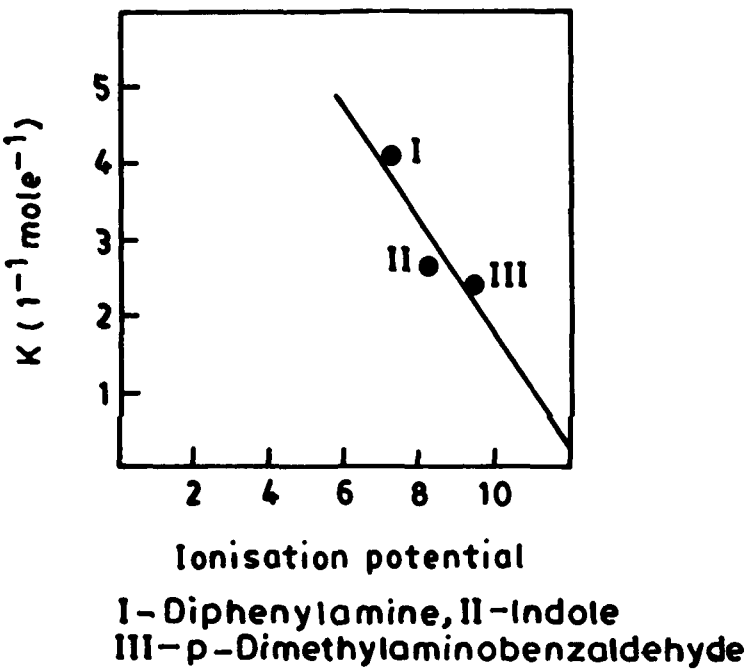

Figure 2.1 : A plot of K for DPA, Indole and pDAB complexes with DNT at 15°C and ionizaiton potentials of DPA, Indole and pDAB.

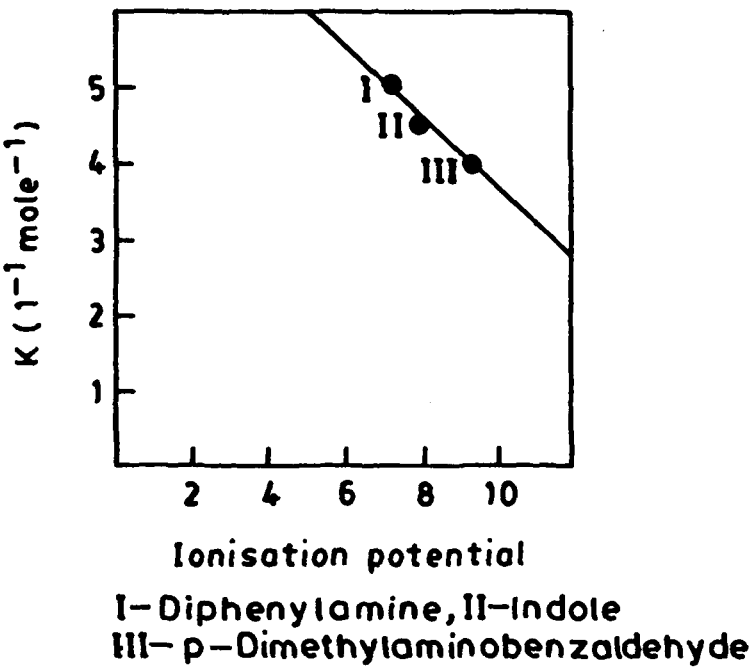

Figure 2.2 : A plot of K for DPA, Indole and pDAB complexes with DNT at 30°C and ionizaiton potentials of DPA, Indole and pDAB.

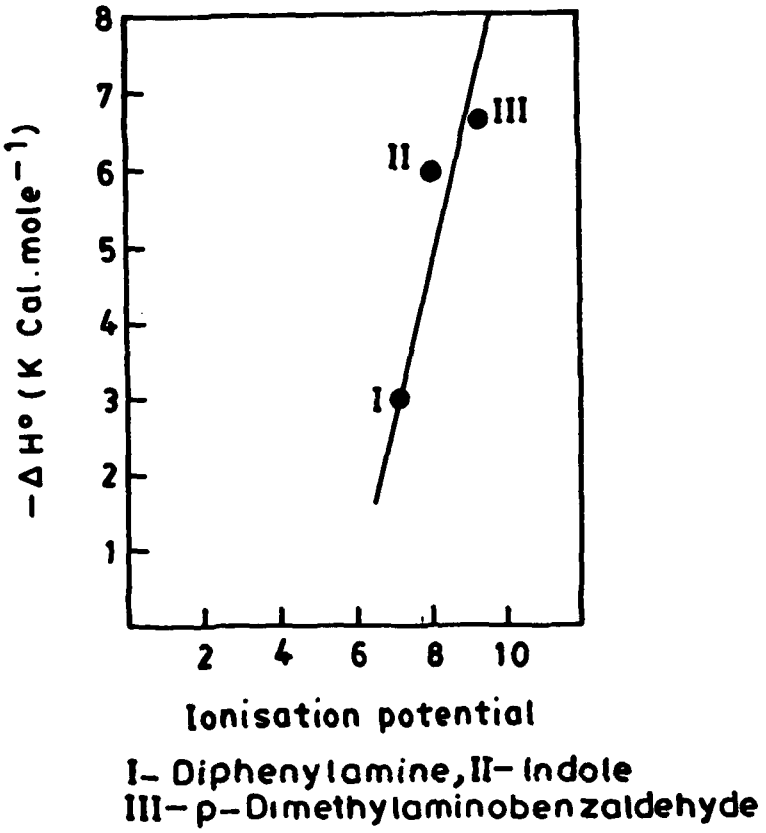

Figure 2.3 : A plot of $-\Delta H^0$ and the ionization potential of the donors (DPA. Indole and pDAB).

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CHAPTER - 3

ISOLATION OF CHARGE-TRANSFER BAND OF DINITROTOLUENE - DIPHENYLAMINE SYSTEM
INFLUENCE OF SOME ALKALI METALS AND ALKALINE EARTH METALS ON CHARGE-TRANSFER COMPLEXATION

Charge-transfer complex interactions have been a source of much controversy. One of the important controversies is whether charge-transfer or hydrogenbonding predominates in those systems which are capable of both [1,2]. The colour reaction of DNT with DPA has been studied and a mechanism was postulated. Spot tests for DNT and other explosives were developed by treatment with DPA and observing the colour in the u.v. light [3]. Malone [4] has described the detection of hydrazines and amines with nitrocompounds including DNT. Unfortunately the chemistry of these reactions has not been given. A systematic study of DNT-DPA reaction may therefore provide a theoretical basis for the analytical applications cited above and it may also lead to a model for the reactions of the antibodies with other acceptor.

A search of the literature shows that relatively few studies have been reported on the charge transfer complexes of DNT. Buchler and Heap [5] prepared the molecular compounds of DNT with α-naphthylamine, naphthalene and benzidine and reported the melting points, the stoichiometry and the colour of these compounds.

Sometime ago Nabi *et.al.* had been involved in developing methods using polynitro aromatics as reagents or test substances [6-8], DNT is an important polynitro aromatic having a very potent hepatocarcinogen activity [9]. The very fact that it causes cancer of the liver specifically gives significance to this compound. Some dinitrocompounds have important pharmaceutical properties [10].

DNT was chosen because DNT is a non-conventional acceptor. As methyl group in DNT is normaly electron releasing, by the hyper-

conjugative effect it fortifies the electron-donating ability of DNT. The effect of the elctron-withdrawing nitro group is thereby diluted and DNT act as an acceptor, and there is a possibility of the formation of charge transfer complexes [11].

The present study was therefore undertaken to investigate the mechanism of the reaction of DNT with DPA system and the effect of alkali and alkaline earth metals on the complex probably for the first time.

EXPERIMENTAL

DNT (FLUKA) and DPA (BDH, Analar) were used after crystallization to constant melting points. DMSO (BDH, Analar) was used as such. All the Alkali nitrate ($LiNO_3$, $NaNO_3$ KNO_3) and Alkaline earth nitrates {$Mg(NO_3)_2$, $Ca(NO_3)_2$, $Sr(NO_3)_2$} are from E. Mark GR were used as such. Solid state study was made by the capillary method developed by Rastogi [12]. Reflectance spectra of the reactants and of the product obtained by intimately mixing the reactants in different mole ratios in the solid state, were recorded. The UV-visible spectra were recorded from 200 to 500 nm on Bausch and Lomb spectronic 1001 UV-visible spectrophotometer. The association constants were evaluated under the condition that the donor concentration was kept in far excess over the acceptor concentration.

RESULT AND DISCUSSION

DNT is an unusual acceptor in many ways. The electron releasing effect of the CH_3 group compensates partly for the

electron withdrawing effect of the nitro groups and therefore DNT shows weak acceptor properties. Buchler and Heap [5] isolated the molecular organic compounds of m-dinitrobenzene, DNT and 2,4-dinitrophenol and determine their melting points. They noted that the least number of molecular compounds are formed with DNT.

In the solid state a charge-transfer band is obtained with a maximum at 300 nm (Figure-3.1). It is a featureless broad band arising from the charge transfer from the no bond to the dative structure of Mulliken [13] i.e. π-π^* transition. The jobs method at 300 nm shows that the complex in the solid state is formed in the mole ratio 1:1 (Figure-3.2).

To complement the solid state studies some experimetns were also performed in the solution state using UV-visible spectroscopic technique. The charge-transfer band was isolated by the method of Mulliken and Reid [14] in the 80:20% DMSO : H_2O solvant and is given in figure-3.3.

Equilibrium constant measurements were carried out at λ_{420}. The equaiton used was, the well known Benesi-Hildebrand equation [15].

$$\frac{[A]_0}{A} = \frac{1}{K\,\varepsilon_{420}} \cdot \frac{1}{[D]_0} + \frac{1}{\varepsilon_{420}} \qquad \text{.....(1)}$$

Under the condition $[D]_0 >> [A]_0$. $[D]_0$ in equation 1 signifies the initial concentration of donor (DPA). $[A]_0$ is the initial concentration of acceptor (DNT) and A is the absorbance of the complex. A plot of $[A]_0/A$ vs $1/[D]_0$ is linear with the slope equal to

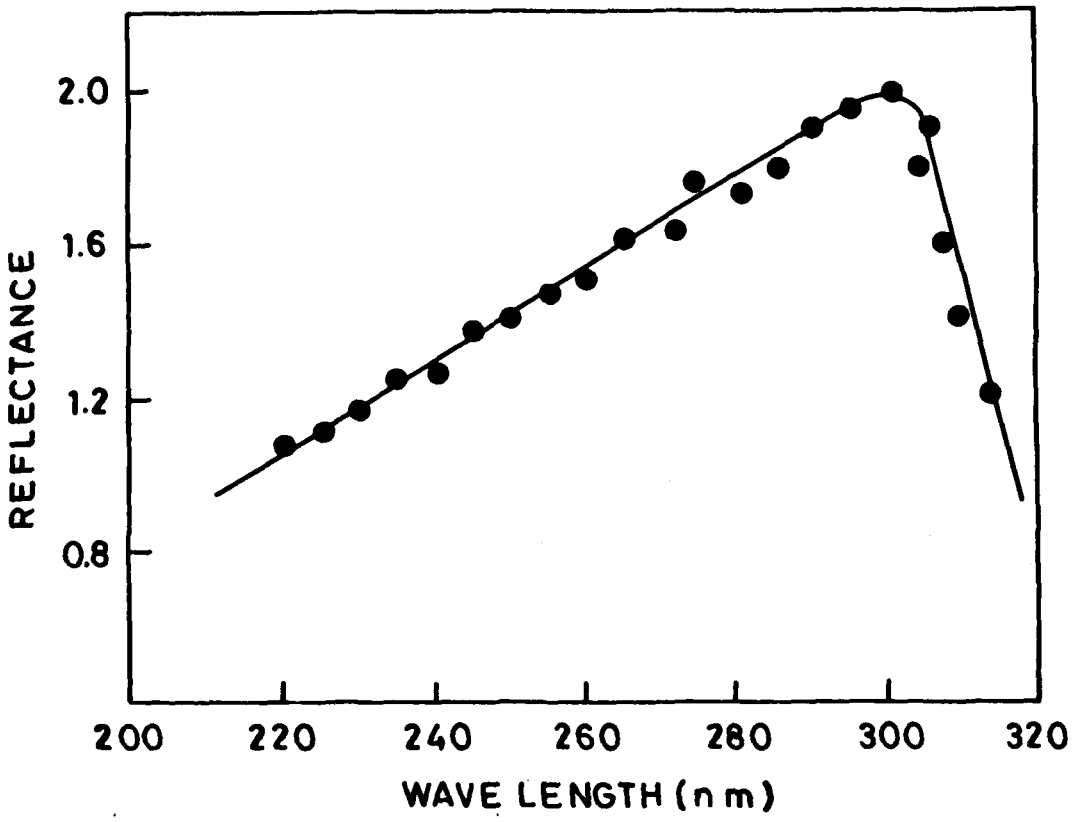

Figure 3.1 : The charge transfer band of DNT-DPA complex isolated in the solid state.

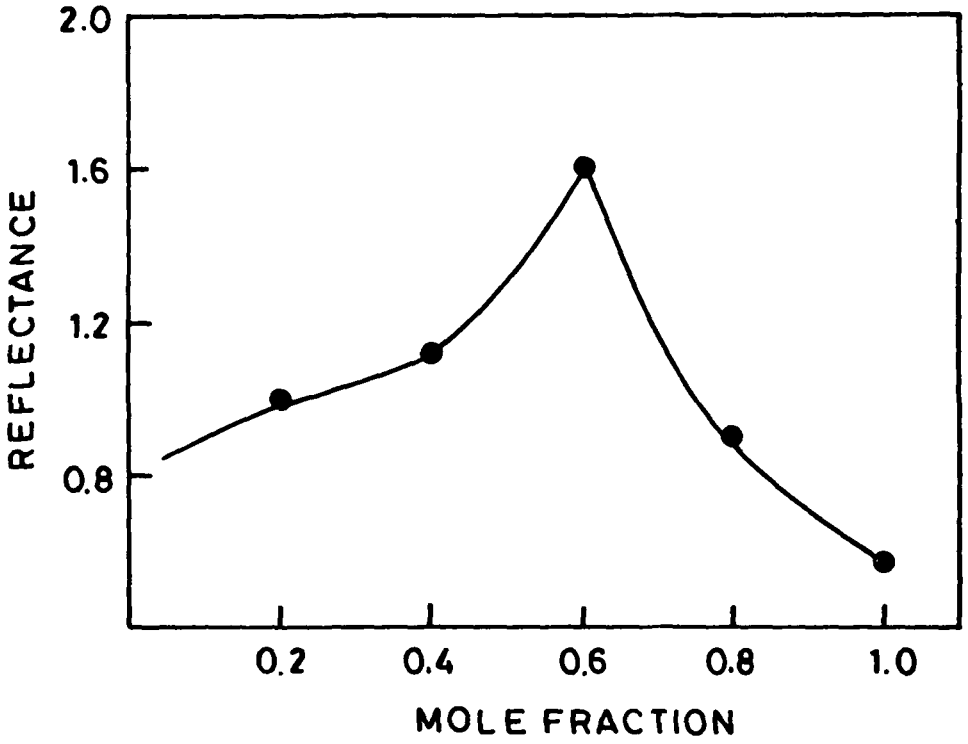

Figure 3.2 : Job's plot for the system DNT-DPA in the solid state.

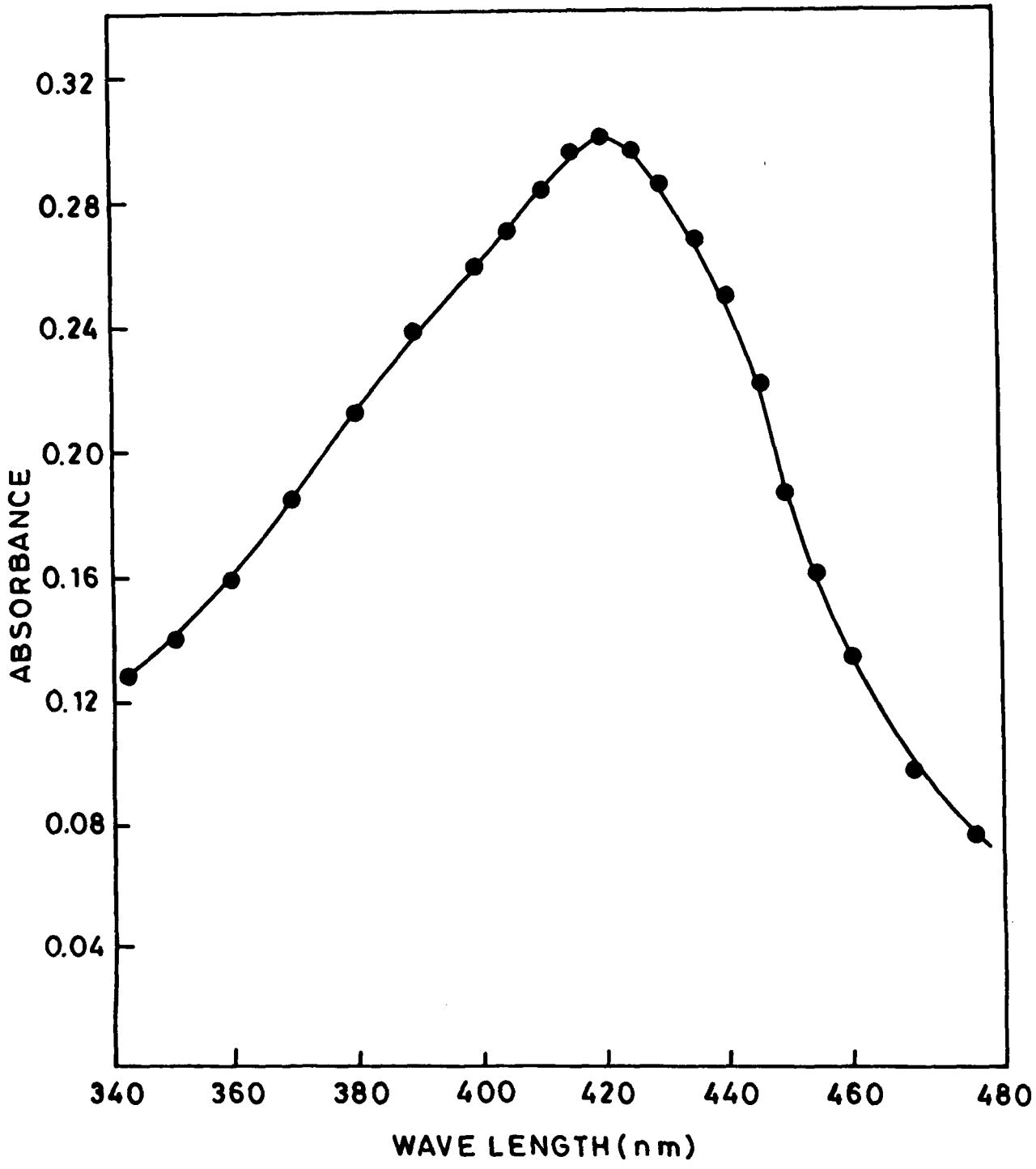

Figure 3.3 : The charge transfer band of DNT-DPA complex in 80:20% DMSO:H_2O solvent. (Complex structure)

1/K ε_{420} and the intercept $1/\varepsilon_{420}$. The association constant (K) is then obtained by dividing the intercept by the slope.

The reaction product in the solid state is a charge-transfer (π - π^*) complex being stabilized further by the localized interaction between the non bonding electrons of the donor NH group and the NO_2 group of the aceptor. The charge-transfer band has been isolated in the solid state and the solution phase.

The theoretical model which explains most of the properties of charge-transfer complexes and the one which is widely accepted is the one given by Mulliken [16]. According to Mulliken the wave equation for a charge-transfer complex has the form.

$$\psi_N(AD) = a\ \psi_0(A,D) + b\ \psi_1\ (A^- - D^+).$$

The wave function ψ_0 has been termed by Mulliken the "no bond" function. One possible configuration of the complex is given in Figure - 3.4.

In presence of cations a blue shift in frequence occurs between DNT and DPA charge transfer complex in 80:20% DMSO : H_2O mixture. The intensity also increase sharply. Sometimes there is some overlap with the CT band and consequent difficulty in obtaining information about the shifted visible band. This blue shift is illustrated in Table 3.1 for DNT-DPA in presence of some alkali and alkaline earth metals in decreasing of their ionization energy. This change is often enough to make possible determination of equilibrium constants of complexes. A rough overall summary of changes in the visible band of DNT-DPA complex in presence of

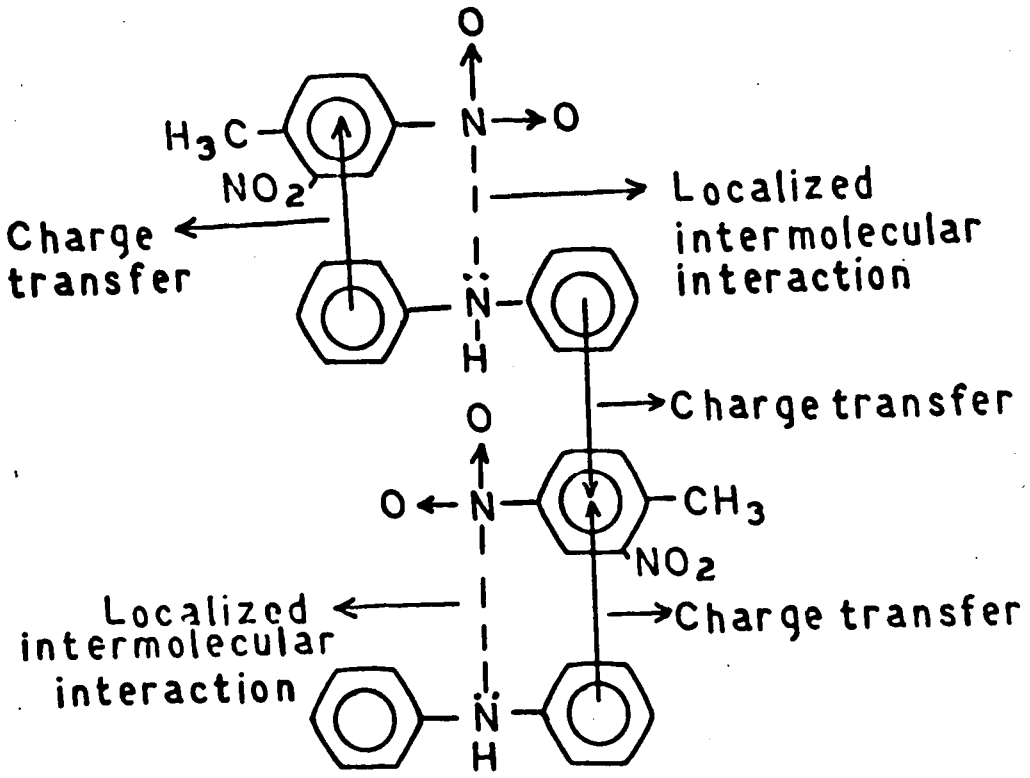

Figure 3.4 : Proposed structure of DNT-DPA complex.

metal ions is presented in Table 3.1.

Ionisation potential energy of Li, Na, K, Mg, Ca and Sr is plotted against $\overline{\nu}_{CT}$ give straight line. The ionization potential are from reference [17]. Nevertheless it can be seen in Fig. 3.5-3.8, an approximate linearity is found between ionization potentials and wave number. It is taken as a confirmation of charge-transfer complexes. This observation is similar to that found by McConnell, Ham and Platt [18] and by Hastings, Franklin, Schiller and Matsen [19] for iodine charge-transfer complexes.

The value of Ionization potential obtained by extrapolation are particularly questionable, yet the correspondence of such values with theoretically obtained values is often surprisingly good. Indeed this might be expected that the ionization of cation is effecting the donor potentialities of the complexes.

Equilibrium constant measurements were carried out at λ_{max} in the presence of different cations by Benesi-Hildebrand equation [15]. The trend of data in Table 3.1 further confirms the charge-transfer chemistry of DNT-DPA system and charge-transfer complex of DNT-DPA system in presence of cations are more stable than that in the absence of these cations.

The interaction of an alkali metal M, an odd donor of low ionization potential, with a π acceptor of high electron affinity results in essentially complete electron transfer to form an odd-even ion pair $A^- M^+$. Donor acceptor interactions which result in ion pairs can conveniently be called ionogenic. Complex of this type are less familiar and are called non-conventional charge transfer complex.

TABLE - 3.1

THE CHARGE TRANSFER BANDS AND ASSOCIATION CONSTANT (K) OF DNT-DPA WITH PRESENCE OF SOME ALKALI AND ALKALINE EARTH METALS

S.N.	System	λ_{Max}	$K_{eq.}$
1.	DNT-DPA	420	0.80
2.	DNT-DPA-Li	400	0.82
3.	DNT-DPA-Na	397	1.20
4.	DNT-DPA-K	392	1.34
5.	DNT-DPA-Mg	390	1.38
6.	DNT-DPA-Ca	405	0.33
7.	DNT-DPA-Sr	409	0.30

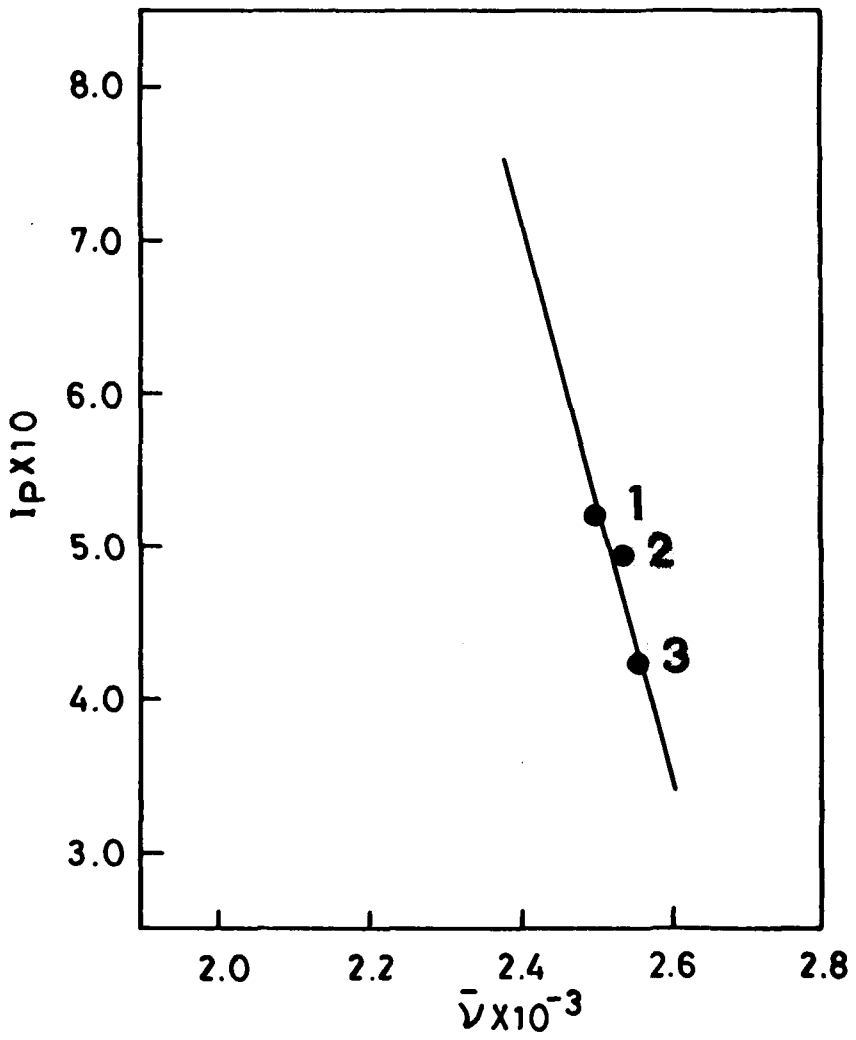

Figure 3.5 : Correlation between the $\bar{\nu}_{CT}$ and the first ionization potentials of (1) Li, (2) Na (3) K.

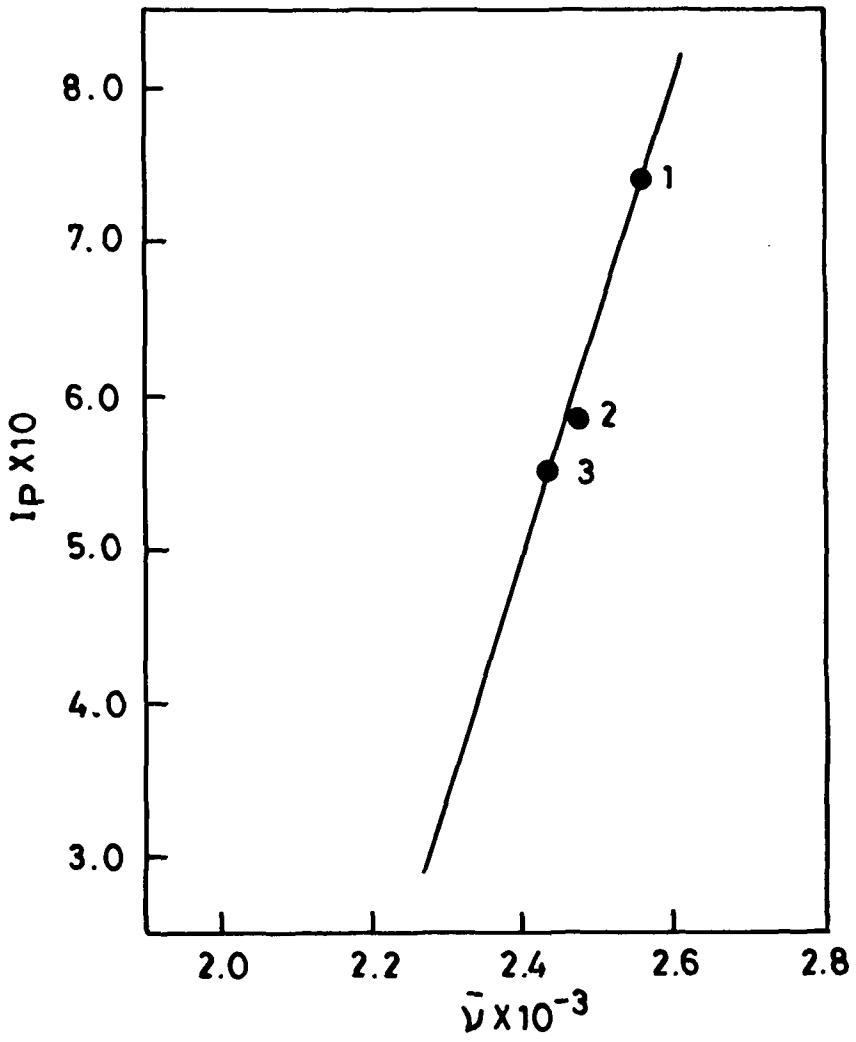

Figure 3.6 : Correlation between the $\bar{\nu}_{CT}$ and the first ionization potentials of (1) Mg; (2) Ca; (3) Sr.

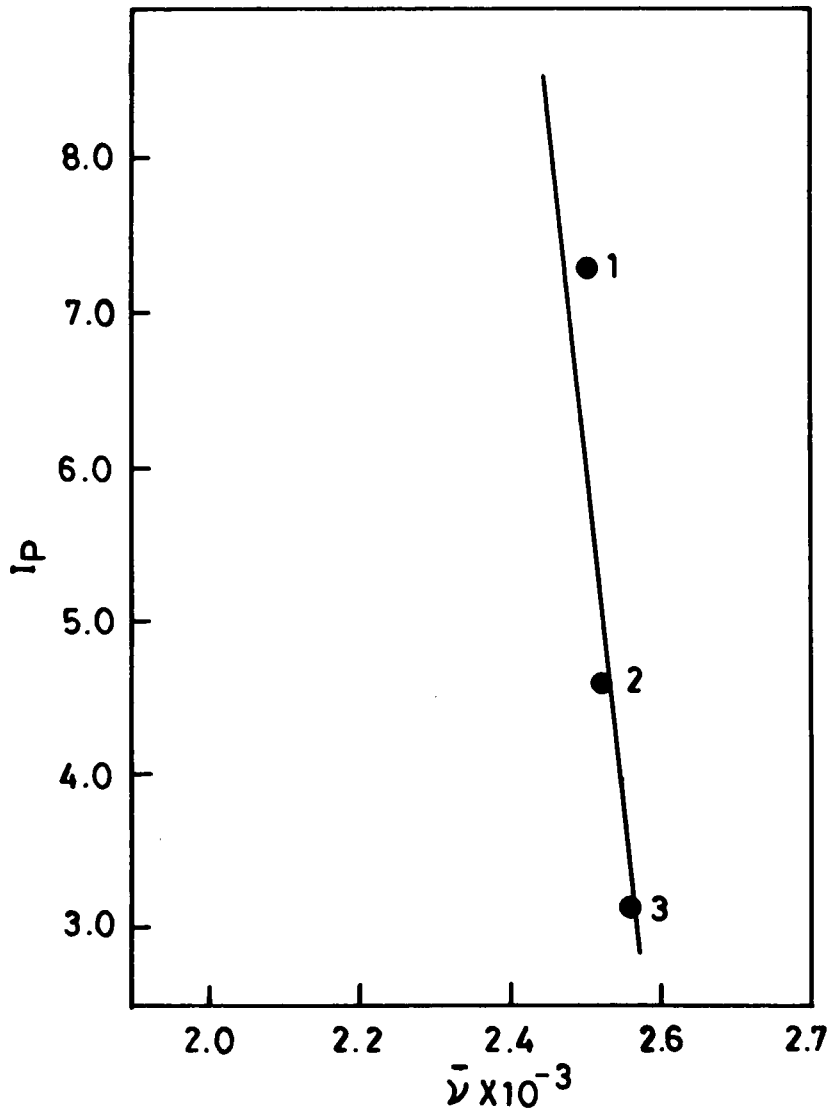

Figure 3.7 : Correlation between the $\bar{\nu}_{CT}$ and the second ionization potentials of (1) Li; (2) Na, (3) K

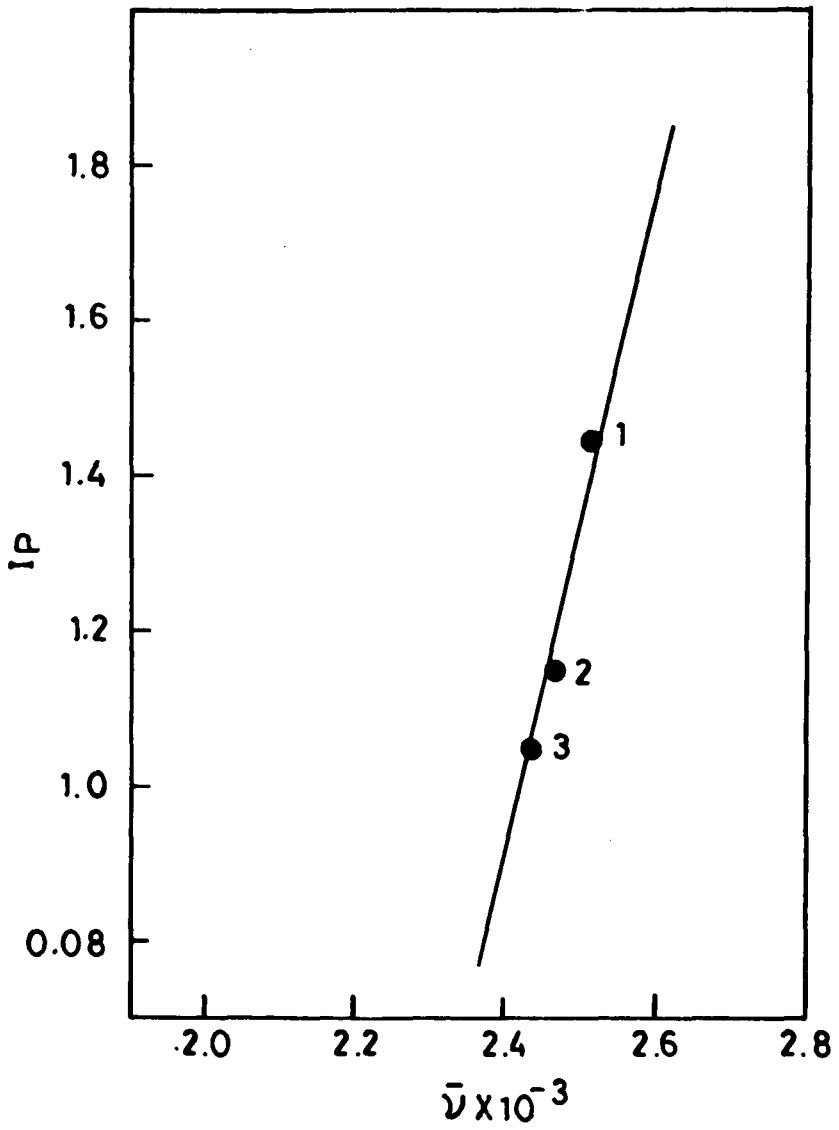

Figure 3.8 : Correlation between the $\bar{\nu}_{CT}$ and the second ionization potentials of (1) Mg; (2) Ca, (3) Sr.

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CHAPTER - 4

QUANTITATIVE DETERMINATION OF SOME POLY-NITROAROMATIC COMPOUNDS VIA THEIR MOLECULAR COMPLEXES WITH DIPHENYLAMINE

Polynitroaromatics are important polutants and almost all show carcinogenic activity. A new method has been generalized for the quantitative determination of polynitroaromatics via their molecular complexes with diphenylamine. Molecular complex interaction has been a source of much controversy. One of the important controversies is whether, the complex owing to charge-transfer or hydrogen bonding predominates in those systems which are capable of both [1,2]. Although spectrophotometric and kinetic methods of analysis enjoy great popularity, the corresponding methods based on molecular complexes have been largely neglected. These methods can facilitate the determination of even those substances that give strongly overlapping, or identical maxima. By use of these methods, specificity can be introduced in those cases where there is an identical colour. Even for analysis based on systems that attain equilibrium rapidly. Beer's Law has been indiscriminately applied to obtaine ε_{λ} values. It is now clear that in such instances a direct determination of ε_{λ} cannot be made because the degree of dissociation of the complex in solution is usually significant [3]. An alternative method for evaluating ε_{λ} in such instances is described below. Kinetic method obviously cannot be applied to the analysis.

Methods based on molecular complexes are therefore proposed to remove such anomalies and to analyse nitrocompounds, which is otherwise not easily achieved owing to their unstable and identical colours.

Usually such methods have been used for the determination

of electron donors (often drug molecules). In the present work the process has been reversed and here electron acceptor (polynitroaromatics) has been determined due to lack of suitable methods.

EXPERIMENTAL

Nitrobenze, 1,3, dinitrobenzene and diphenylamine were BDH AnalaR reagents (Merk Ltd.). 1,2,-dinitrobenzene, 1,4-dinitrobenzene and 2,4-dinitrotoluene were from Fluka while 3,5-dinitrobenzoic acid are 1-chloro-2,4-dinitrobenzene were from E. Merck (Darmstadt, Germany).

The GR and AnalaR reagents were used as received. Other reagents were recrystallised till their melting points were in agreement with reported values.

The reagent diphenylamine is a weak aromatic amine and a non-conventional donors as it has two phenyl groups. It is a carcinogen, perhaps more toxic than aniline. It has a relative molecular mass of 169.23, a boiling point of 302°C, a melting point of 54.5°C, a density of 1.160 and marked solubility in Ethanol, diethyl ether, acetone, benzene and dichloromethane. The latent heat of fusion is 25.23 and the heat of vaporization 15.64 cal g^{-1} (105.56 and 65.44 J g^{-1}, respectively). The dimagnetic susceptibility is 109.7 ($^{-}\chi$ mol X 10^{6}).

The solvents used were CCl_4(B.D.H.), dichloromethane (Merck Ltd.) and Ethanol (B.D.H.). All analysis were carried out on a Bausch and Lomb spectronic 1001 UV-visible spectrophotometer and spectronic 20 spectrophotometer.

The nitro compound (0.012 - 0.019 mg), dissolved in the appropriate solvent (1 ml), is treated with diphenylamine (0.8 - 0.08 mol l^{-1}) in the same solvent, mixed well and the mixture allowed to stand for 7 min. The yellow solution is transferred to a suitable spectrophotometric cell and the absorbance at 420 nm measured. The charge-transfer bands are difficult to locate as the nitro compounds absorb very intensely at wavelength below 400 nm and hence cannot be compensated for. Therefore on optimum wavelength (420 nm) was chosen at which nitro compounds did not absorb at all and the sensitivity for the analysis was at a maximum.

Equilibrium constants (K) were evaluated at 420 nm by employing different concentrations (known) of the polynitroaromatics (test substance).

The association constants were evaluated under the condition that the donor concentration were kept in far excess over the acceptor concentration and applying the equations and procedures mentioned below.

Various equations are known for the evaluation of the equilibrium constants (K) of molecular complexes by optical method. The first and the most popular was proposed by BENESI and HILDEBRAND (4) and takes the form :

$$\frac{[A]_0}{A} = \frac{1}{K\varepsilon_{420}} \cdot \frac{1}{[D]_0} + \frac{1}{\varepsilon_{420}} \qquad \text{.....(1)}$$

where $[A]_0$ = initial concentration of acceptor (nitroaromatics) $[D]_0$ = initial concentration of donor (diphenylamine). ε_{420} = molar

absorptivity of the complex at 420 nm, and A= absorbance of the complex. $[D]_0$ was in the range from 0.8 to 0.08 mol l^{-1} and $[A]_0$ was in the range 0.007 to 0.009 mol l^{-1}. $[A]_0$ fixed a constant for one particular set of measurements while $[D]_0$ was varied. According to equation 1 a plot of $[A]_0/A$ vs $1/[D]_0$, under the condition that $[D]_0 >> [A]_0$ should be linear with the intercept giving $1/\varepsilon_{420}$ and the slope equal to $1/K\varepsilon_{420}$. A typical graph is shown in Fig. 4.1. It is true that under the condition $[D]_0 >> [A]_0$, some amount of species AD_2 may be formed.

Therefore, the method of Foster [5], where $[A]_0 = [D]_0$ might be preferable. However, the Benesi-Hildebrand method requires that A should be fully complexed; moreover, the low solubilities of the polynitroaromatics in the solvents used preclude the use of this method.

Once reliable values of K and ε_{420} have been obtained by the Pushkin-Varshney-Kamoonpuri equaiton [6].

$$\frac{1}{A} = \frac{1}{K\varepsilon_{420}} \cdot \frac{1}{[A]_0} \cdot \frac{1}{[D]_0} + \frac{1}{\varepsilon_{420}} \cdot \frac{1}{[A]_0} \qquad \text{.....(2)}$$

is applied to samples of the acceptor whose concentration is not known and $[A]_0$ evaluated

A graphy of 1/A v/s $1/[D]_0$ should be linear with a slope equal to $1/K\varepsilon_{420}$ X $1/[A]_0$ and an intercept equal to $1/\varepsilon_{420}$ x $1/[A]_0$. The slope is a constant because $[A]_0$ is a constant. K and ε_{420} values are fed into the slope of equation 2 from equation 1 and $[A]_0$ evaluated. The use of Pushkin-Varshney-Kamoonpuri. equation

is advantageous here as the method requires that $[A]_0$ should be unknown. In the case of the Benesi-Hildebrand equation, $[A]_0$ would have to be known. A typical plot is shown in Fig. 4.2 and Fig. 4.3.

RESULTS AND DISCUSSION

Although all nitro compounds give yellow coloured complexes, they can be made specific by evaluating K, which will be a characteristic constant for the particular test substance. K and ε_{420} values are reported in Table 4.1. By evaluating $[A]_0$ the medhod can be used for the quantitative analysis of A, which are shown in Table 4.2.

The major emphasis of this chapter is on the method. And therefore the sensitivity of the method has not been a crucial consideration here. However, it is evident that the method can be applied easily to trace analysis as well.

Most methods for the spectroiphotometric determination of polynitroaroamtics suffer from the disadvantage that the colours produced are unstable or non-specific.

The interaction of diphenylamine with polynitroaromatics seems to be a case of non-conventional charge-transfer complexes. In the case of 3,5-dinitrobenzoic acid, where ethanol is used as the solvent. It is possible that the colour is due to a coloured intermediate rather than a molecular complex.

The method may find use in quantitative thin-layer chromatography (TLC), especially charge-transfer chromatography, and could be used in quantifying biological

material for polynitroaromatics before actual sampling or in water pollution studies, specially in polluted waters from effluents of the explosive industry. Although these analytes have a complex matrix, analysis of the polynitroaromatics after seperation by paper chromatography or TLC may be feasible.

TABLE - 4.1

DONOR		DIPHENYLAMINE		
ACCEPTOR	**SOLVENT**	λ_{CT}(nm)	K mol^{-1} $liter^{-1}$	ε_{420}
1,2,-dinitrobenzene	CH_2Cl_2	420	0.98	155.00
1,3-dinitrobenzene	CCl_4	420	0.46	920.08
1,4-dinitrobenzene	CH_2Cl_2	420	0.90	293.90
2,4-dinitrotoluene	CCl_4	420	0.32	938.41
Nitrobenzene	CCl_4	420	0.60	166.67
1-Chloro-2,4-dinitrobenzene	CCl_4	420	0.80	373.75
3,5-dinitrobenzoic acid	C_2H_5OH	420	1.22	466.00

TABLE - 4.2

COMPOUNDS	$[A]_0$ mol liter^{-1}		
	Taken	Found	Error (%)
1,2,-dinitrobenzene	0.008	0.0080	0.00
1,3-dinitrobenzene	0.008	0.0079	± 1.25
1,4-dinitrobenzene	0.008	0.0081	± 1.25
2,4-dinitrotoluene	0.008	0.0078	± 2.50
Nitrobenzene	0.008	0.0081	± 1.25
1-Chloro-2,4-dinitrobenzene	0.008	0.0079	± 1.25
3,5-dinitrobenzoic acid	0.008	0.0078	± 1.25

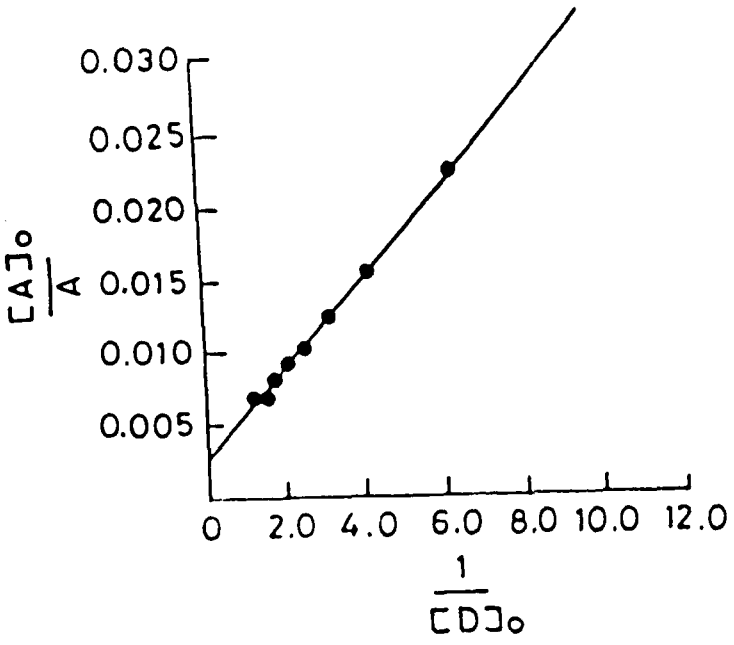

Figure 4.1 : The Benesi-Hildebrand plot for the evaluation of K and ε_{max} with a known concentration of acceptor for the 1-chloro-2,4-dinitrobenzene-diphenylamine system.

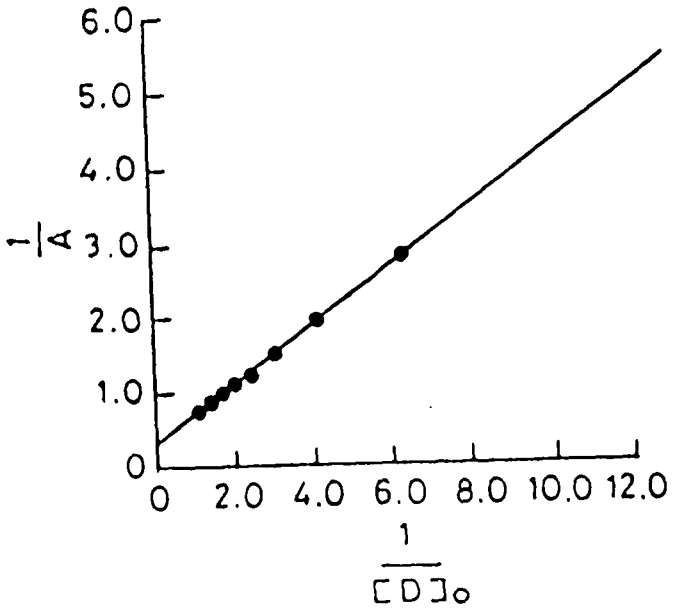

Figure 4.2 : The Pushkin-Varshney-Kamoonpuri plot for the evaluation of $[A]_0$ (unknown), for the 1-chloro-2,4-dinitrobenzene-diphenyl-amine system.

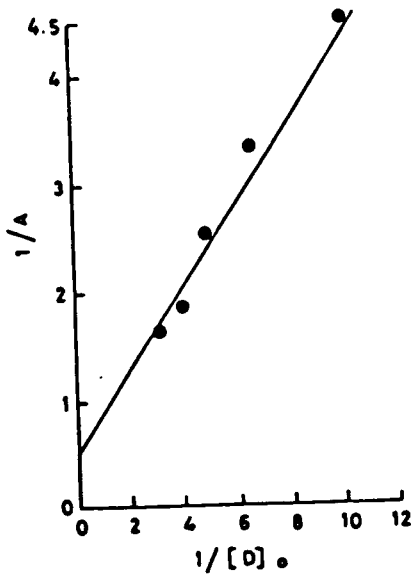

Figure 4.3 : Plot for the evaluation of K by the PVK equation for the 2,4-dinitrotoluene-diphenylamine system.

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CHAPTER - 5

MULTIPLE CHARGE-TRANSFER BANDS IN COMPLEXES INVOLVING ORGANOMETALLIC DONOR CORRELATION OF SPECTRAL ABSORPTION DATA WITH Z-VALUES

Since the classical experimental work by Benesi and Hildebrand [1] on the absorption spectra of mixtures of electron donors and acceptors, and the theoretical description of the results in terms of charge-transfer (CT) by Mulliken [2], there has been continued unabated interest in CT complex, and a wide variety of donor-acceptor systems have been investigated [3,4]. Until recently, in the use of π-donor-π-acceptor systems, almost all studies have been concerned with simple 1:1 complexes, which usually associate very weakly in solution. Recent interest in molecular complexes involving organometalic donor-acceptor compounds which exhibit direct charge-transfer (CT) emission or absorption spectra. Some important studies on organometallic donors have been carried out recently [5-9].

Some charge-transfer complexes show two or three charge-transfer bands in their absorption spectra. The appearance of such multiplet charge-transfer bands has been ascribed to the difference between the donor and acceptor orbitals involved in charge-transfer. Briegleb, Czekalla and Reuss [10] have shown that the energy difference between the first CT band and the second CT band is approximately equal to the excitation energy of the donor cation in the case of the chloranil complexes and the tetracyno-ethlene (TCNE) complex which involve polycyclic aromatic hydrocarbons as the electron donor. The second CT bands in these cases can be assigned to the excitation associated with the charge from the second highest occupied orbitals of the donor to the lowest vacant orbital of the acceptor. This interpretation, however, raises a question about the configuration of the complex. It is generally believed that a donor molecule takes an orientation relative to an acceptor molecule so as to give a maximum

overlapping between the highest occupied orbital of the donor and lowest vacant orbital of the acceptor. Such a structure is most favourable for the appearance of the first CT band, but it is not necessarily favourable for the second one, since the symmetry of the second highest occupied orbital is usually different from that. In the case of napthalene - TCNE complex also shows multiple CT bands [11].

The objectives of the present investigation were (1) to study the multiple charge-transfer bands appeared in the complex of 1-chloro-2,4-dinitrobenzene (CDB) – triphenylantimony (TPA), (2) to determine the effect of solvent on the energies of these transitions and a new correlation for multiple charge-transfer band is proposed here.

EXPERIMENTAL

Triphenylantimony was A.R. Grade from Fluka and 1-Chloro-2,4-dinitrobenzene was G.R. Grade from E. Merck (Germany). Both the reagents were used as received. All solvents (CCl_4, $CHCl_3$, CH_2Cl_2, $(CH_3)_2 C = 0$, CH_3OH and C_2H_5OH) were from AnalaR, BDH. Pool England. UV-visible studies were carried out on Bausch and lomb spectronic 1001 spectrophotometer.

RESULTS AND DISCUSSION

1-chloro-2,4-dinitrobenzene and triphenylantimony form a yellow coloured charge-transfer complex in CCl_4. The UV-visible spectrum was recorded by Mulliken method [13].

The absorption maxima for 1-chloro-2,4-dinitrobenzene and triphenylantimony complex here measured in six different solvents and are shown two maxima bands (Fig. 5.1-5.6). The band multiplicity may arise from

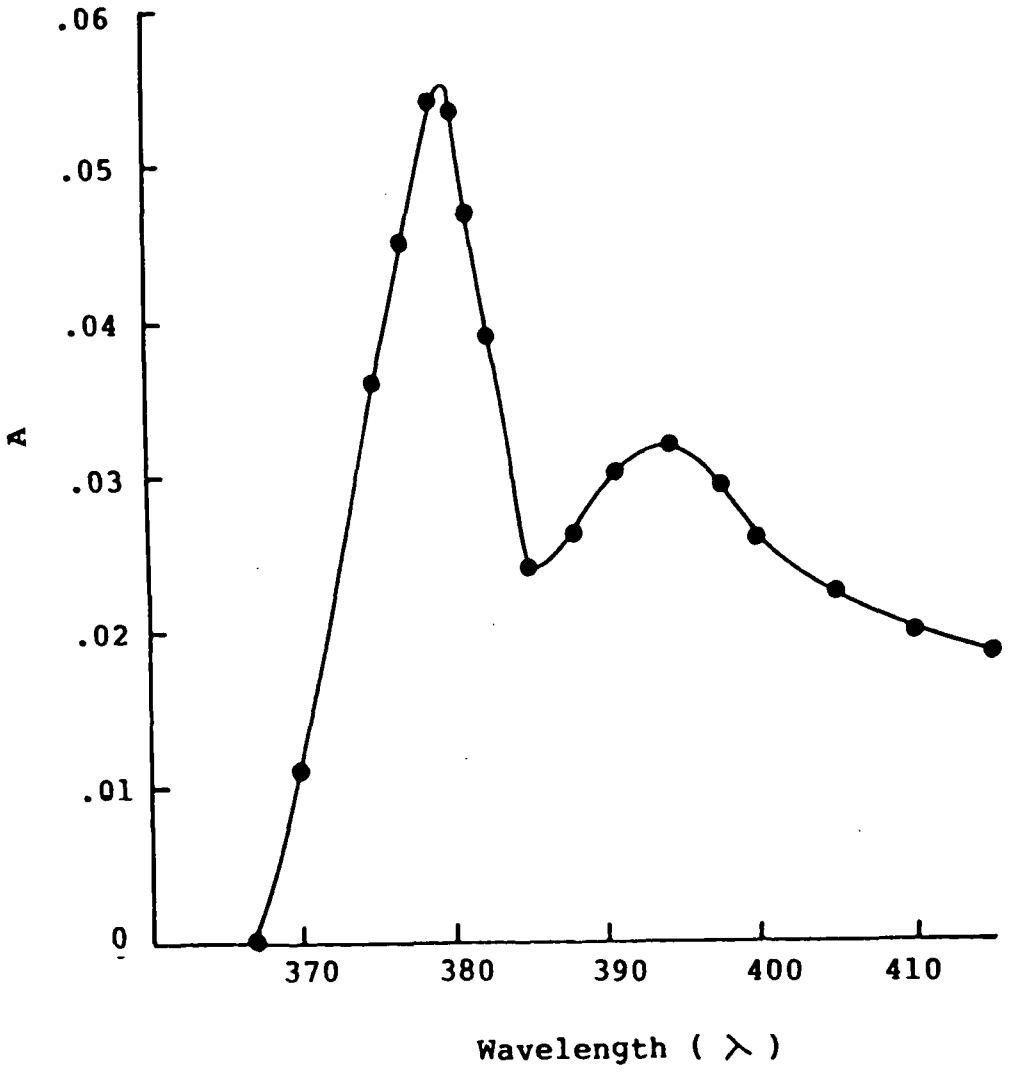


Figure 5.1 : The Multiple charge-transfer bands of triphenylantimony-1-chloro-2,4-dinitrobenzene complex in CCl_4.

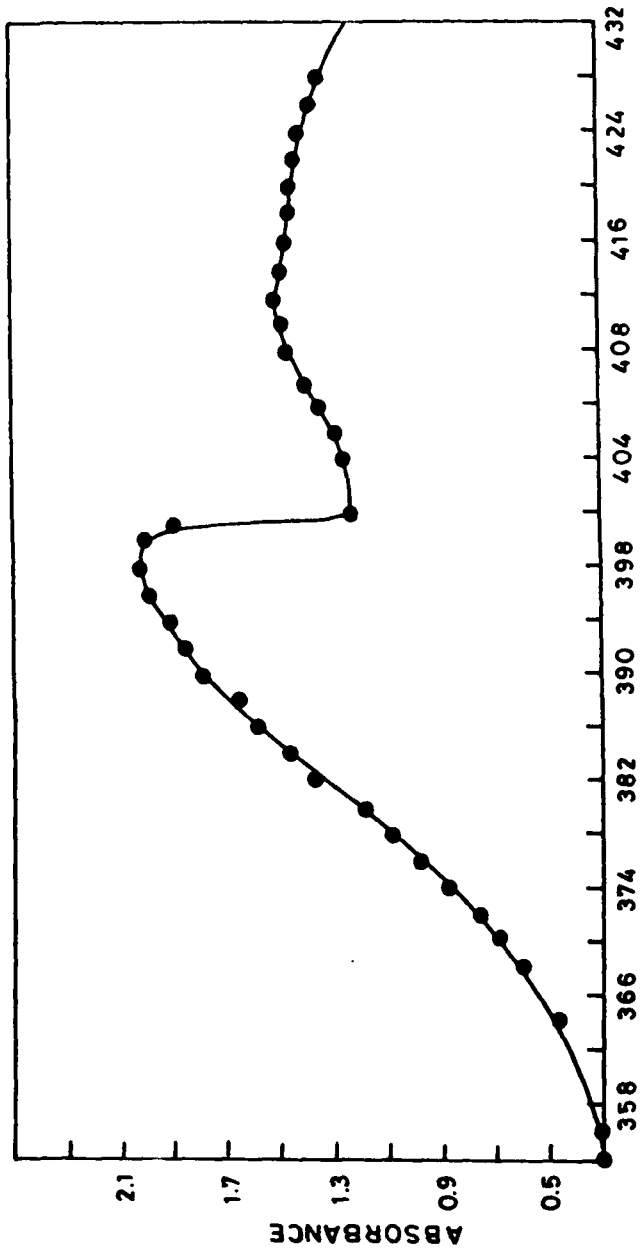


Figure 5.2 : The Multiple charge-transfer bands of triphenylantimony-1-chloro-2,4-dinitrobenzene complex in $CHCl_3$

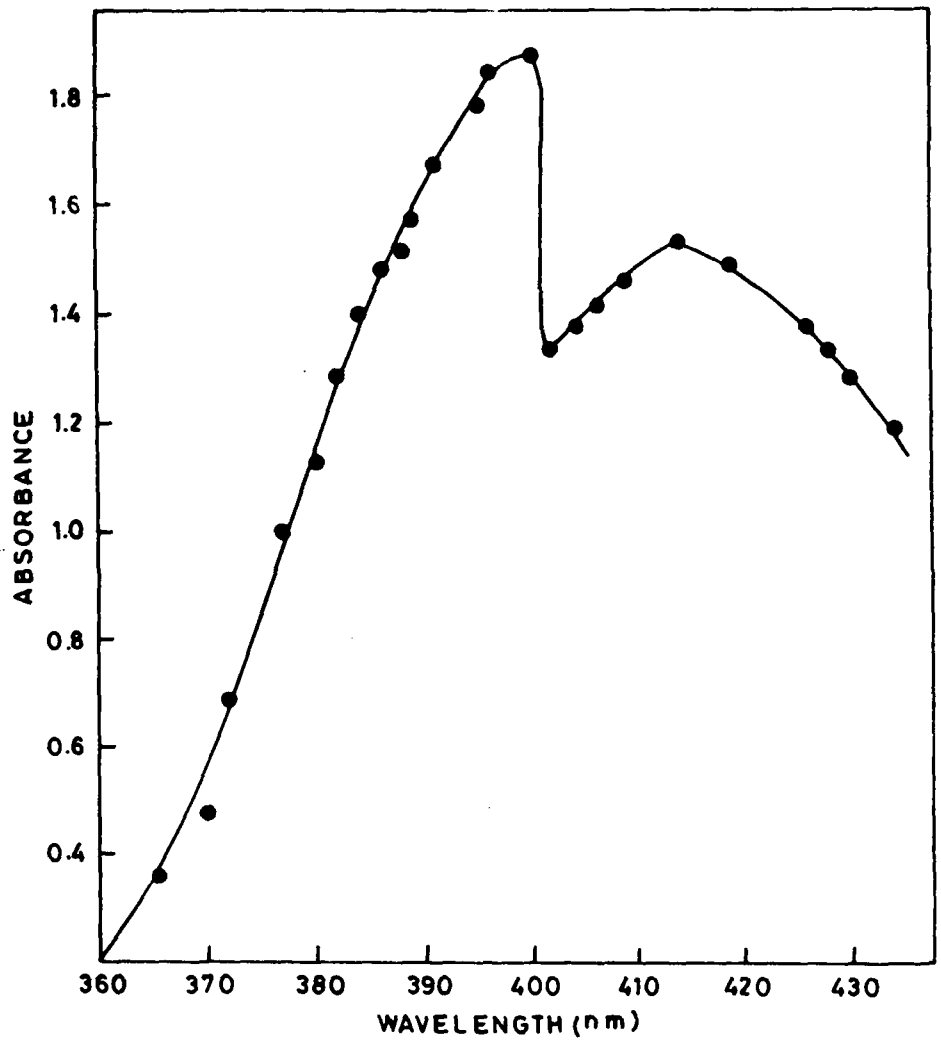


Figure 5.3 : The Multiple charge-transfer bands of triphenylantimony-1-chloro-2,4-dinitrobenzene complex in CH_2Cl_2

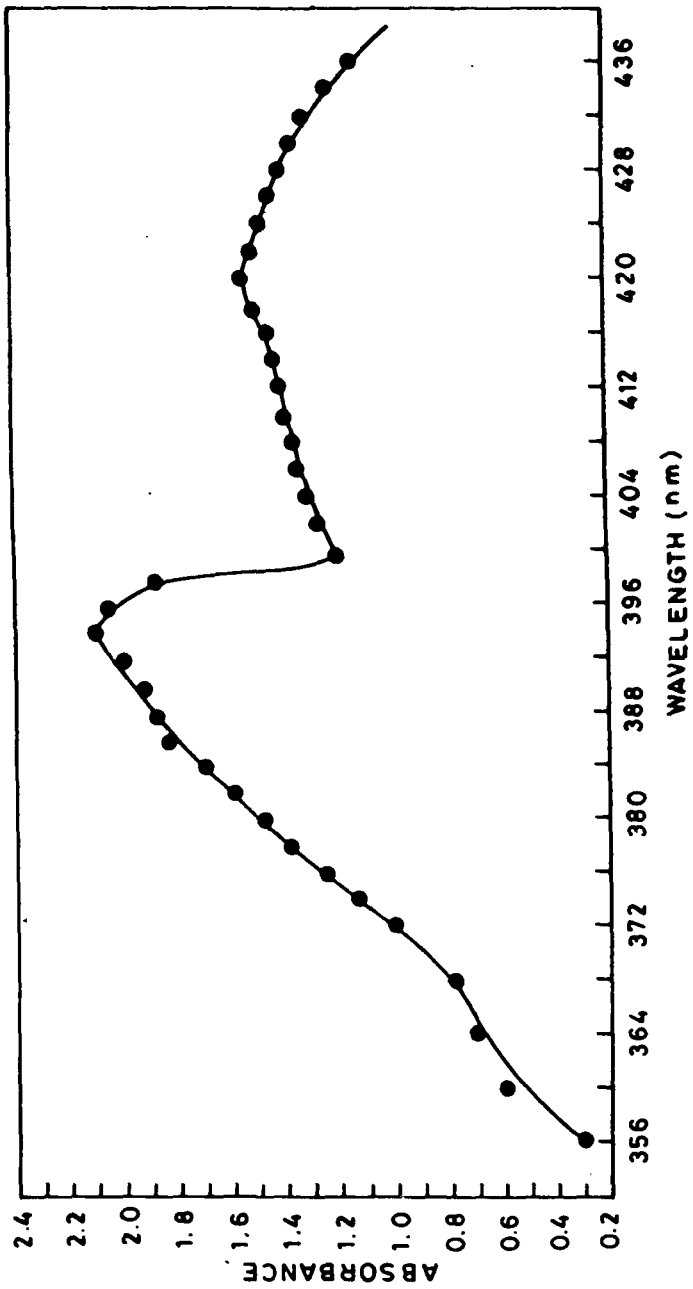


Figure 5.4 : The Multiple charge-transfer bands of triphenylantimony-1-chloro-2,4-dinitrobenzene complex in $(CH_3)_2$ C = O

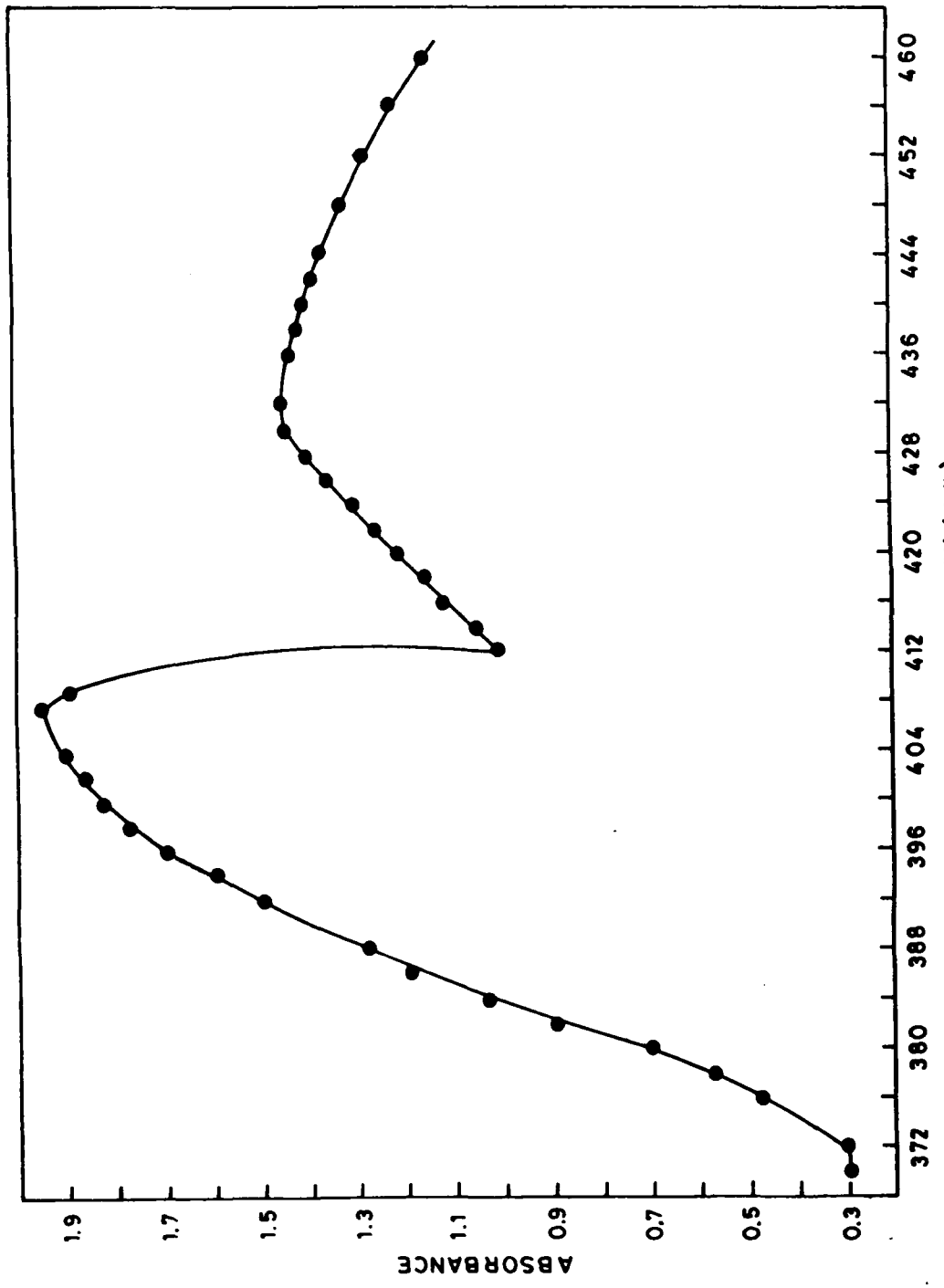


Figure 5.5 : The Multiple charge-transfer bands of triphenylantimony-1-chloro-2,4-dinitrobenzene complex in C_2H_5OH.

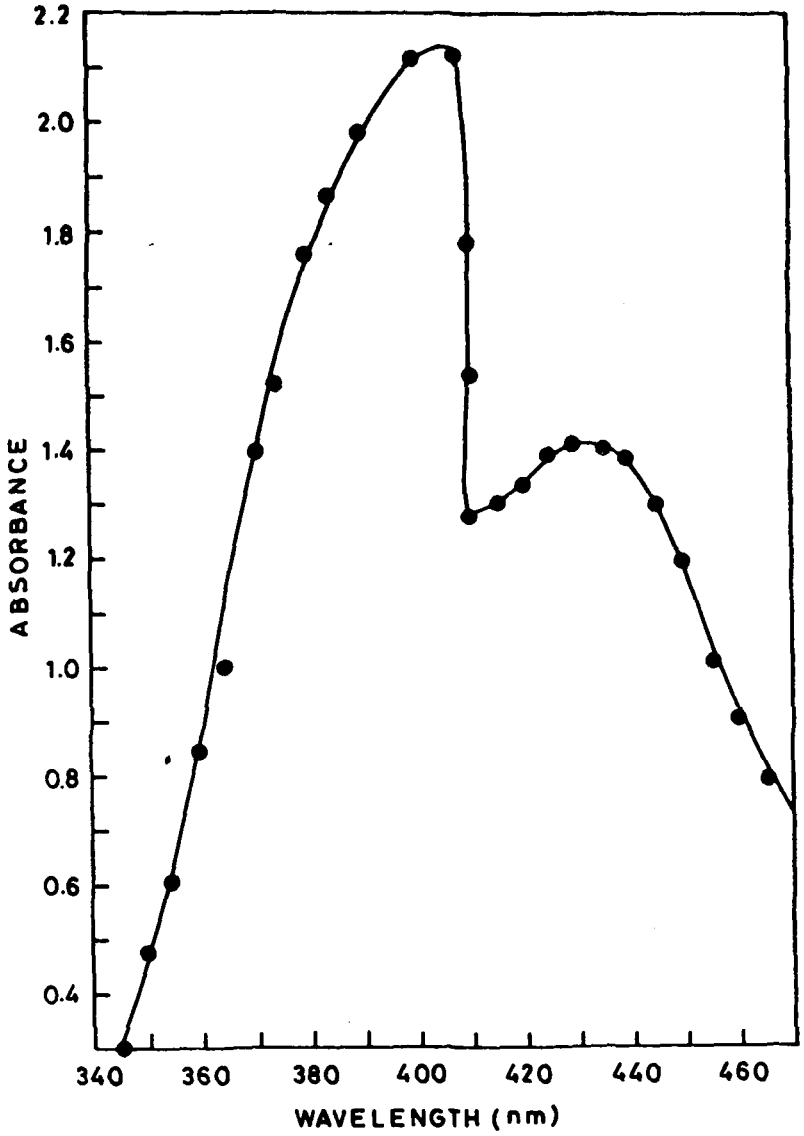


Figure 5.6 : The Multiple charge-transfer bands of triphenylantimony-1-chloro-2.4-dinitrobenzene complex in CH_3OH.

electron donation from more than one energy levels in the donor to more than one energy level in the acceptor. Gott and Maish [14] suggested that in the presence of isomers which are different in the mutual orientations of the symmetry axes of the donor and acceptor has also been assumed an explanation of the multiple charge-transfer bands. Latter on Zweig [15] confirmed this theory. According to McGlynn two isomeric complexes are formed if the maximum overlap principle is applied [16]. Solid state and IR studies [17] have been done between 1-chloro-2,4,dinitrobenzene and triphenylantimony. As per Kross [18] classification IR study indicate that in addition to π-π^* bonding there is a localized intermolecular interaction is probably due to the contribution of the metal to the complex [17].

The IR spectra of several related organometallic compounds illustrated tht the metal-C bands lie somewhere close to 1400 cm^{-1}. So, that the band at 1430 cm^{-1} in free TPA is due to Sb attached to a phenyl ring. A band in this position is not present in spectrum of CDB. In the complex this peak shifts to 1435 cm^{-1}; again showing a shift of 5 cm^{-1} toward lower frequency as in the case of nitro asymmetric stretching band. This shift also confirmes that a weak charge-transfer complexation.

Association constant K was evaluated by the method of Foster [26] under the condition $[A]_0 = [D]_0$ and applying the equation

$$\frac{[A]_0}{A} = \frac{1}{K\varepsilon_\lambda} \cdot \frac{1}{[D]_0} + \frac{2}{\varepsilon_\lambda}$$

where $[A]_0$ is the initial concentration of acceptor equal to $[D]_0$, the initial concentration of the donor, A is the absorbance of the complex at λ, K is the association constant and ε_λ is the molar absorptivity of the

complex at λ. On plotting $[A]_0/A$ Vs $1/[D]_0$ for a series of solutions a straight line is obtained under the condition $[A]_0 = [D]_0$ with the slope equal to $1/K\ \varepsilon_\lambda$ and the intercept equal to $2/\varepsilon_\lambda$.

EFFECT OF SOLVENT ON UV-VISIBLE SPECTRUM

A number of investigators [18] have observed solvent effects on UV-Visible spectra which are associated with charge-transfer phenomena. Kosower [19-22] has interpreted changes in spectra with solvent in terms of the relative polarities of the ground and excited states. For molecular complex formation, the effect of the solvent will depend on whether the reactants or the complex are preferentially stabilized or the complex are preferentially stabilized by solvation [23]. Weiss has predicted that charge-transfer complexation will be favoured by increasing the polarity of the medium. This is based on the fact that the reactants, are in most cases unchanged while the complex has a contributing structure with a charge seperation [24].

The equilibrium constants for formation of 1-chloro-2,4-dinitrobenzene and triphenylantimony complexes at the first band at which the equilibrium constants (K) were calculated for a series of six solvent are given in Table 5.1 and in Fig 5.7 the equilibrium constants are plotted agaisnt the dielectric constant of the solvents. As can be seen from Fig. 5.1 equilibrium constant is a linear function of dielectric constant. This type of correlation has shown by Ross et.al. [25].

In order to compare the observed maxima with solvent polarity, the maxima were converted into transition energy by means of the relation (derived from $E = h\nu$), E_T (Kilocalories/mole) = $2.859 \times 10^{-3}\ \nu$ (in cm^{-1}). Table 5.2 shows the two charge-transfer bands with their transition

TABLE - 5.1

SOLVENT	K	Dielectric Constant(D)
CCl_4	9.88	2.238
$CHCl_3$	9.72	4.806
CH_2Cl_2	9.01	9.08
$(CH_3)_2$ C=O	8.80	15.40
C_2H_5OH	8.12	24.30
CH_3OH	3.79	33.62

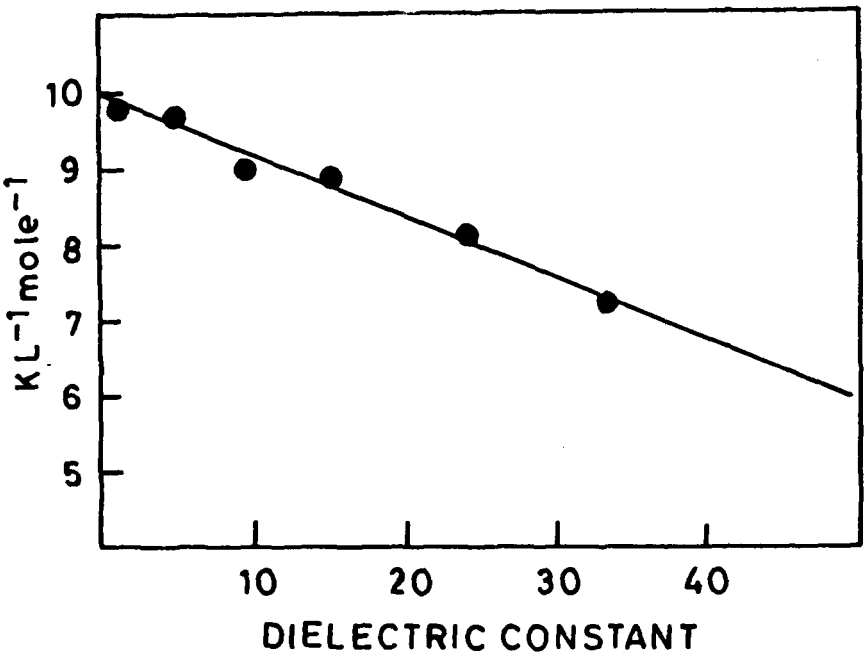


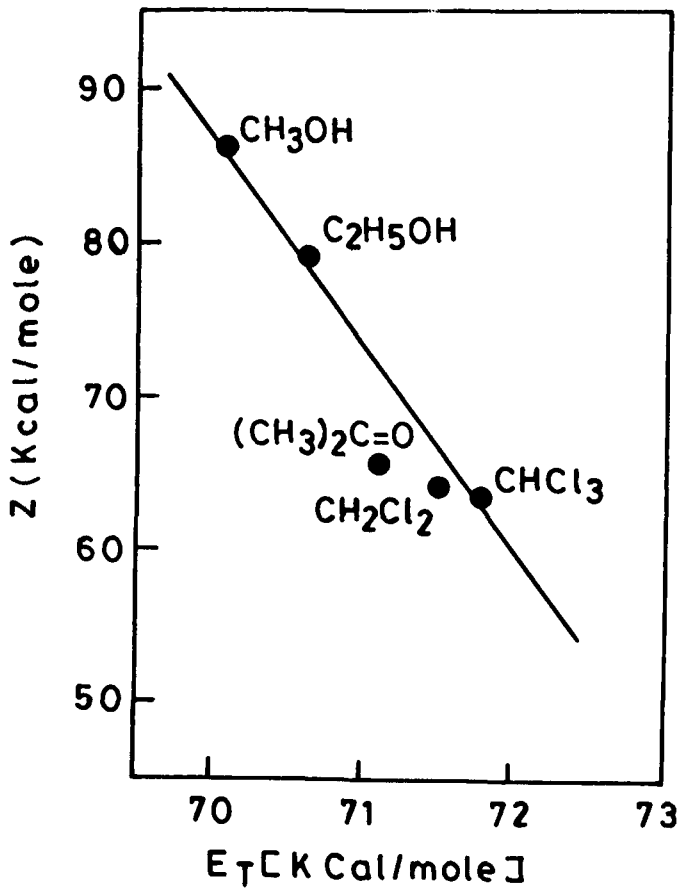
Figure 5.7 : A plot of K for triphenylantimony/1-chloro-2,4-dinitrobenzene complex in six different solvents and the dielectric constant of the solvents.

TABLE - 5.2

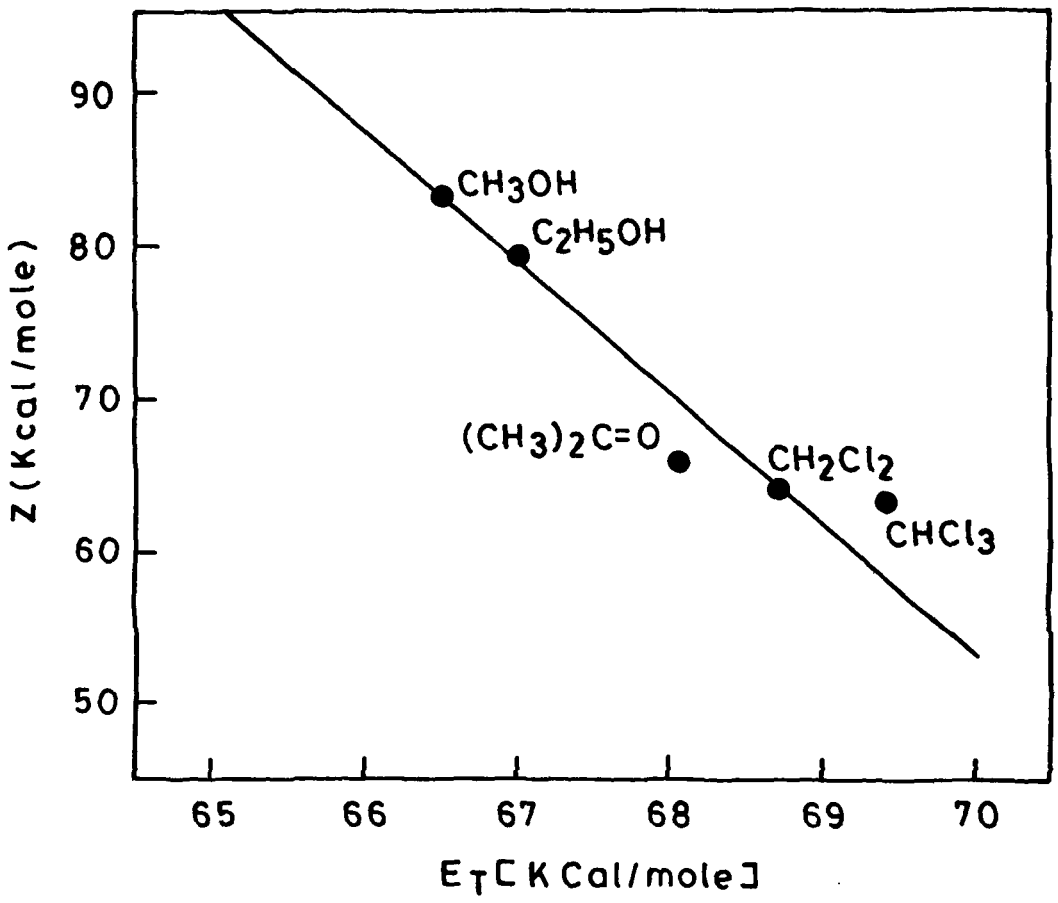
SOLVENT	Z Value	TRANSITION - I		TRANSITION - II		ΔE_T
		λ	E_T	λ	E_T	
CCl_4		389	73.496	395	72.569	1.117
$CHCl_3$	63.2	398	71.834	412	69.393	2.440
CH_2Cl_2	64.2	400	71.475	416	68.725	2.75
$(CH_3)_2C=O$	65.7	395	71.119	421	68.071	3.048
C_2H_5OH	79.6	405	70.592	426	67.112	3.48
CH_3OH	83.6	408	70.073	430	66.489	3.584

energy (E_T) and transition energy difference (ΔE_T) of two bands. The transition energy of first and second charge-transfer bands are plotted against Z-values (empirical measurements of solvant polarity). Z-values as taken from reference [26]. (Figs. 5.8 and 5.9). The curve shows a linear relationship between them.

One new correlation between ΔE_T and Z (Fig. 5.10) for multiple charge transfer bands was shown a very good linear relationship. The good linearity of the graphy is clear from the value of the correlation coefficient which is equal to 0.9999 for the figure. In order to ascertain that Z-values were useful for correlating data in different solvents. This relationship will be helpful for confirming the multiple charge-transfer band in different solvants.



5.8 : A plot of transition energy of first charge-transfer band and Z-values of the solvents.



: A plot of transition energy of second charge-transfer band and Z-values of the solvents.

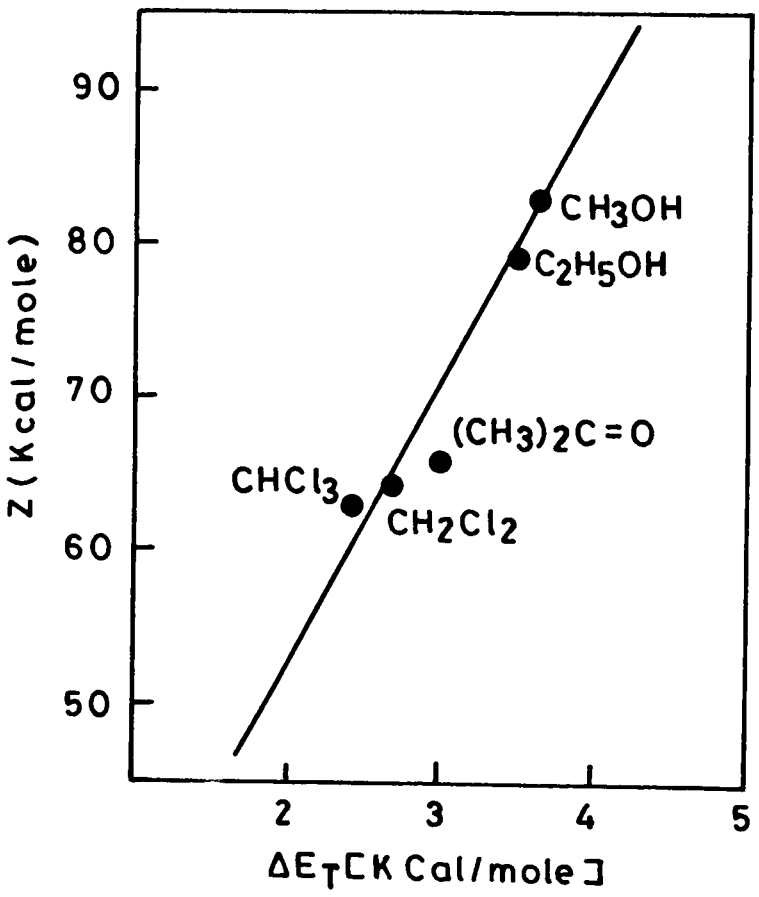


Figure 5.10 : Correlation between ΔE_T and Z-values of solvents.

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CHAPTER - 6

KINETIC EVIDENCE FOR A CHARGE-TRANSFER MECHANISM AND SPECIFIC DETERMINATION OF AN IMPORTANT PHARMACEUTICAL REACTANT 2,4,-DINITROPHENYLHYDRAZINE

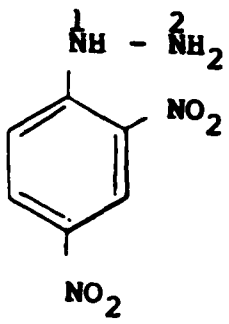
The colours produced when an aliphatic amine is added to a solution of a polynitroaromatic compound have been explained as due to various interactions [1], and even to all of them occurring almost simultaneously. Orvik and Bunnett [2] supported the view that the colours are due to formation of anionic sigma-complexes and was confirmed by the studies of Fyfe et al. [3,4]. Though this interpretation may hold for this particular system, it is not necessarily applicable to all aliphatic amines-polynitroaromatic systems. It is known [5] that a non-polar solvent such as cyclohexane and polar aprotic solvents such as dimethylsulphoxide (DMSO), tertiary aliphatic amines form charge-transfer complexes with 1,3,5-trinitrobenzene. Though charge-transfer complexes have been postulated for the corresponding reaction with other aliphatic amines. Nabi *et al.* scanned a number of polynitro-aromatic compounds and found one [6] for which kinetic and other data showed the presence of charge-transfer reaction with aliphatic amines. An aliphatic amine followed by alkali hydroxide has been used in DMSO for the determination of an important polynitro-aromatic compound (2,4-dinitrophenylhydrazine) in the ppm range. The product of decomposition with amine and DNPH alone has been reported earlier [7]. It seems that on adding alkali hydroxide further substitution takes place to give a red coloured anionic sigma complex.

2,4-dinitrophenylhydrazine (DNPH) is an important reagent for a variety of functional group and especially for the carbonyl group. However, it has an important role in various agricultural, biological and pharmaceutical applications. It is used in the

determination of larvicidal activity [8] and in the preparation of herbicides [9]. The effects of dicumarol were investigated in the Ames reversion test by assaying several mutagens including DNPH in the presence of a variety of metabolic systems where it was noted that dicumarol partially prevented metabolic loss of mutagenicity [10]. The structural basis of the mutagenicity of chemicals including DNPH has been studied in *Salmonella typhimurium* [11]. An ion-exchange method has been described for the development of some chemical carcinogens and cancer suspect agents which include DNPH [12]. An improved bioluminescence test for mutagenic agents has been described. All the chemicals including DNPH which are active to the Ames test gave a positive response [13]. A model has been proposed for predicting mutagenicity of organic compounds like DNPH [14]. DNPH has been used for improving service life of engine oil [15]. The mechanism of hepatic megamitochondria formation by ammonia derivatives like DNPH has been studied. [16] HPLC has been used for estimation of aldehydes in blood and tissues via the analysis of their DNPH adducts [17]. A comparison has been made for DNPH and correlation between toxic potency in animals and toxic potency in *Salmonella typhimurium* [18]. DNPH-Uracil compound is an anticancer drug and its anlysis was carried out in pure and dosage forms [19].

2,4-dinitrophenylhydrazine (I) is a non-conventional acceptor as it has a powerful donor group (the hydrazine group), morever it is interesting to uncover whether deprotonation takes place from N^1 or N^2. Recently Qureshi et.al. [20] published for the kinetic and

selective determination of DNPH (as aliphatic amines give similar colours).



In the present study a new specific method for the kinetic analysis of DNPH in its reaction with aliphatic amiens followed by alkali hydroxide in dimethyl sulfoxide (DMSO) is described. This method is superior to other colorimetric methods for polynitroaromatics where unstable colour and a lack of specificity preclude their efficacy.

EXPERIMENTAL

DNPH was a Fluka Guaranteed Reagent and was used as received. n-butylamine was a laboratory reagent obtained from Merck (BDH) and was used without further purification. Dimethylsulfoxide (DMSO) was a Koch Light reagent and was purified by passing simultaneously through a cation exchagner followed by an anion exchanger. All other reagents were of AnalaR grade.

Stock solutions of DNPH (5mg per 10 ml of solvent) were prepared in dimethylsulfoxide and diluted as required. The kinetics of the reaction was studied spectrophotometrically on a Systronics-105 spectrophotometer at a wavelength of 500 nm in a temperature controlled water-bath.

RESULTS AND DISCUSSION

Mixing 0.5 ml of 0.50 mol l^{-1} butylamine with a solution of DNPH generates a deep green colour. The green coloured solution decomposes completely to give a colourless solution by heating in a boiling water-bath for 15 min. On the addition of 1-2 drops of a 4 mol l^{-1} solution of NaOH to the decomposed solution, a deep red colour is generated. The red colour also decomposes with time. The absorbances for decomposition of the red colour were measured at an interval of 30 sec. until the solution again became colourless. Fig. 6.1 shows a graph of 1/A versus time for the decomposition of the red coloured solution.

A plot of the intercepts of the straight lines obtained in Fig. 6.1 Vs concentration of DNPH (in mol l^{-1}) also gives a linear response. The calibration curve is given in Fig. 6.3. By this method

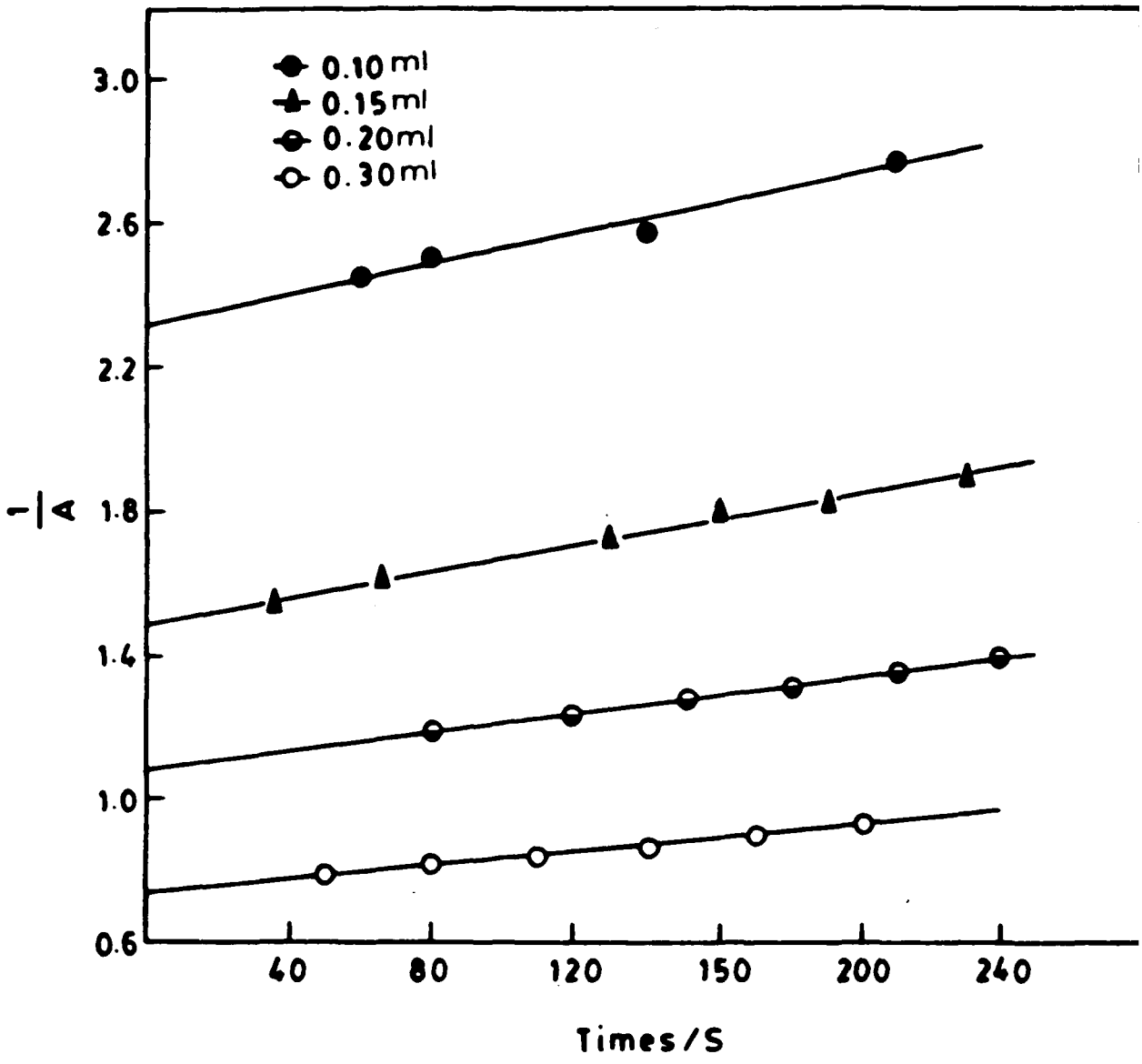


Figure 6.1 : Kinetic plots for the decomposition of the red coloured complex obtained by adding NaOH to decomposed DNPH-aliphatic amine mixture in DMSO at 20°C.
0.20 ml; O, 0.30 ml.

4.9-14.7 ppm of DNPH can be determined.

Absolutely no green colours are observed with carbohydrates [L(+)-arabinose and lactose, D(+)-melezitose [O-α-D-glucopyrasyl-(1 → 3)-β-D-fructofuransyl-α-D-glucopyranside-], glucose, rhamnose and sucrose], acids (acetic, formic, tartaric, phthalic, pyrogallic and oxalic), alcohols (propan-2-ol, ethanol, methanol, 2-methylpropan-2-ol, pentanol, 3-methylbuan-1-ol and 2-methylbutan-1-ol), heterocyclic bases (pyridine), aldehydes (formaldehyde, acetaldehyde, benzaldehyde and p-chlorobenzaldehyde), ketones (acetophenone, cyclopentanone, cyclohexanone, propiophenne and benzophenone), hydrocarbons and their derivatives (benzene, xylene, O-di-chlorobenzene, bromobenzene and toluene), ethers (diethyl, anisole and 1,4-diozan), amino acids (DL-tryptophan, L-lysine, DL-phenylalanine, L-histidine), anilides (acetanilide and benzanilide), nitriles (acetonitrile and benzonitrile), amides (acetamide and benzamide), phenols (phenol, m-cresol and resorcinol) and miscellaneous compounds (chloroform, carbon tetrachloride, urea and thiourea).

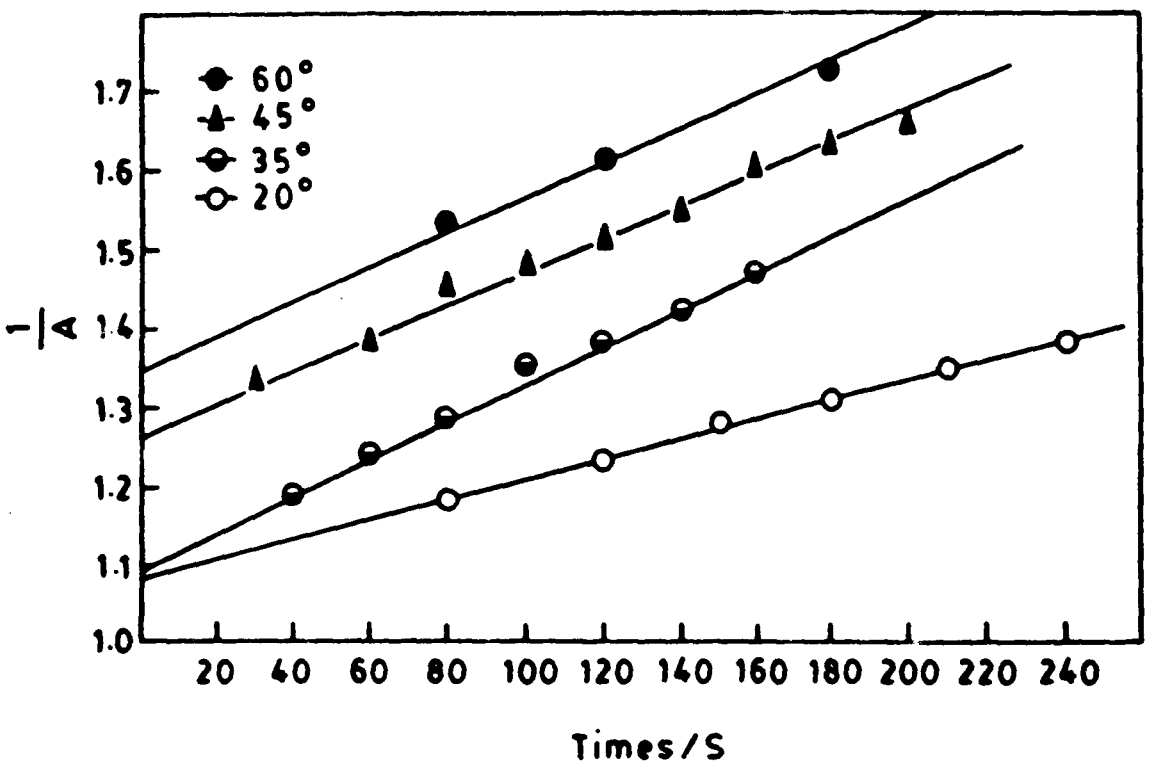
The method is therefore specific for DNPH. The decomposition is faster at elevated temperatures and the effect of temperature is shown in Fig. 6.2.

The product of decomposition with amine and DNPH alone has been reported earlier [7]. The product is shown in Scheme I.

It seems that on adding alkali hydroxide further substitution takes place to give a red coloured anionic sigma complex. The product is shown in Scheme II.

Though the range of the determination is narrow, this factor

is offset by the fact that a specific method has been proposed for an important pharmaceutical reactant where perhaps specific methods do not exist.



6.2 : Temperature dependence of the kinetic plots for the decomposition of the red coloured complex obtained by additing NaOH to decomposed DNPH-aliphatic amine mixture in DMSO, DNPH, 5×10^{-7} mol l^{-1}; n-butylamine, 0.5 mol l^{-1}; sodium hydroxide solution, 4 mol l^{-1}.

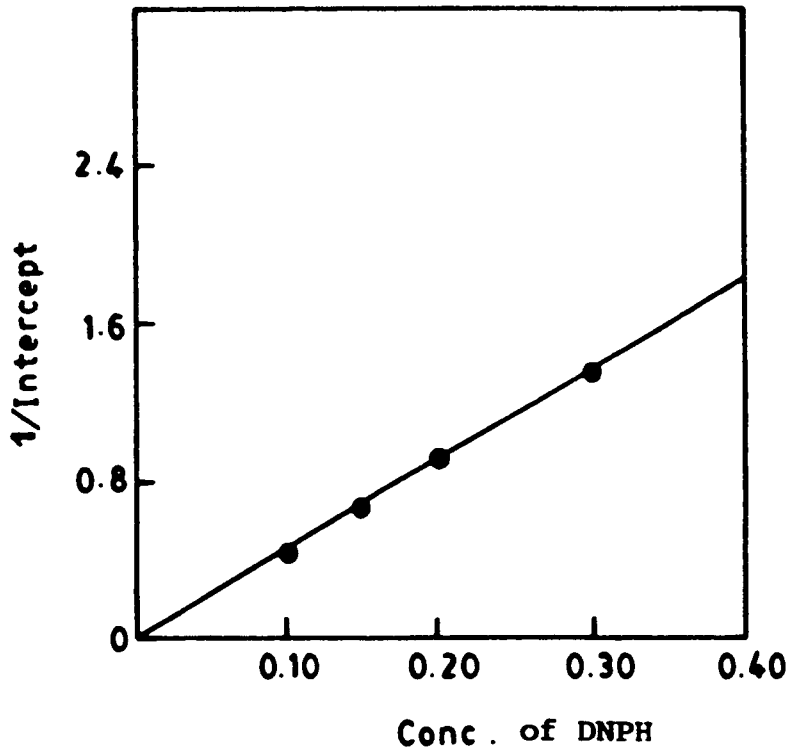
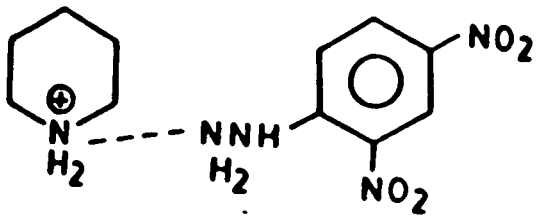
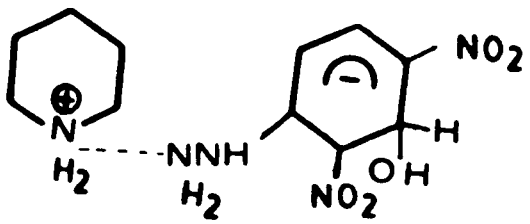


Figure 6.3 : Calibration curve for DNPH.



Scheme I



Scheme II

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